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THE SYNTHESIS AND REACTIONS OF SILYLAZIRIDINES

Thesis submitted by

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for the degree of
Doctor of Philosophy
1997

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Finally, I would like to thank the Almighty God for making this possible.

DECLARATION

Part of this Thesis has been published in the J. Chem. Soc. Perkin Trans. 1996, 327.

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Abstract

The reaction of an α -trialkylsilylvinyl carbanion and carboxylic acid derivatives gives α,β -unsaturated carbonyl compounds which, under the conditions of the reaction undergo further conjugate addition. The enolate thus formed can also react further, depending upon their reactivity and that of the carboxylic acid derivative. The α -trialkylsilylvinyl carbanion reacted with the α,β -unsaturated ketone to give the 1,4-addition product. Further acylation of the enolate by acetic anhydride leads to attack at the oxygen while the use of alkyl chloroformates led to attack at the carbon. The reaction of an α -trialkylsilylvinyl carbanion with the α,β -unsaturated ester, formed a product arising from two conjugate additions, irrespective of the ratio of the carbanion to the ester. This product seems to be particularly stable so does not undergo further acylation.

We also examined the ability of a silicon to stabilise a positive charge in the α - or β -position. Silanes containing both vinyl and allyl groupings (bistrimethylsilylalkene) were synthesised and their reactions with electrophiles were investigated. Our observations show that the silanes prefer to react as allylsilanes.

N-substituted silyl aziridines were synthesised using both thermolytic and photolytic reactions between organic azides and allyltrialkylsilanes. The reaction of allyltrialkylsilanes with bromine azide and the subsequent cyclization of the adduct formed by reaction with lithium aluminium hydride gave the corresponding N-unsubstituted silyl aziridine. The silyl aziridines were shown to undergo ring-opening reactions with nucleophiles by way of attack on either of the aziridine carbons or on the silyl group. Nucleophiles such as hydrogen halides, trimethylsilyl halides and chloroformates react with the aziridines to give only the β -addition product via an " S_N1 "-type process. Whereas the use of sodium azide gave both the β - and α -addition products, with α -addition product (" S_N2 "-type process) being the major isomer. In the " S_N1 " type process, the intermediate β -carbonium ion formed is stabilized by hyperconjugation by the trimethylsilyl group.

Reaction of iodosobenzene with a chlorotrimethylsilylsulphonate ester gave a very reactive electrophilic intermediate which reacted with various alkenes, in a one pot synthesis to give either sultones or cyclic sulphates. The cyclic sulphates were converted to the corresponding N-benzylaziridines.

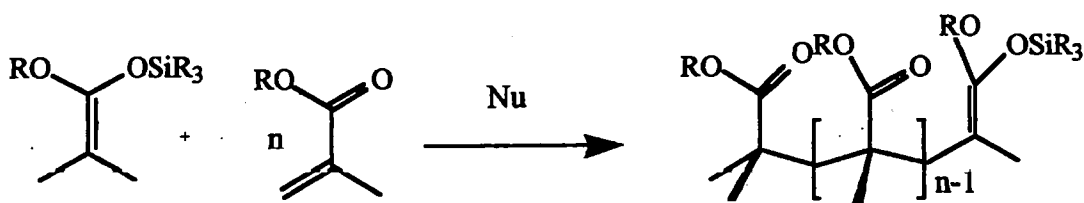
INTRODUCTION

1.1 Organosilicon compounds in organic synthesis

Since the preparation of the first organosilicon compound chlorotriethylsilane, in 1904 by Kipping¹, the trialkylsilyl group has been the subject of much interest in organic chemistry. Initially, it was primarily used to confer volatility to compounds for gas chromatography and to provide characteristic fragmentation in mass spectroscopy^{2,3}. The modern development of organosilicon chemistry as applied to synthesis, really began in the late 1960's. Such compounds are particularly useful as protecting groups⁴ owing to the ease of silylation and desilylation^{5,6,7}. Functional groups such as hydroxyl, amino or thiol can be temporarily protected from undesirable side reactions as the trialkylsilyl derivatives. The stabilising influence of a trialkylsilyl group on carbonium ions in the β -positions⁸ and anions in the α -positions⁹ coupled with their directing effects^{10,11} on substitution and elimination, make organosilicon compounds very powerful synthetic tools. This is enhanced by the ability of the silicon moiety to migrate to electronegative centres¹² and of the silicon atom to increase its co-ordination number¹³. The use of organosilicon groups to direct and control the stereochemical outcome of reactions is exemplified by the work of Stork in the early 1970's.

He employed α -trimethylsilylvinylketones to solve a long standing problem in synthesis namely the regiospecific trapping of specific enolates generated in aprotic solvents, and therefore under non-equilibrating conditions, to direct annulation reactions¹⁴. Stork also showed that trimethylsilyl enol ethers are effective precursors to regiospecific lithium enolates¹⁵. Silicon compounds can further serve to enhance the reactivity of some reagents. This is clearly illustrated by group transfer polymerisation, where the silyl ether

group initiates the chain polymerisation reaction¹⁶ (Scheme 1.1).



Scheme 1.1 Group transfer polymerisation

The preparation of several heterocyclic compounds has been achieved via the silyl derivatives¹⁷.

1.1.1 Physical properties of organosilicon compounds

A comparison of the chemistry of silicon and carbon is useful to fully understand and predict the behaviour of organosilicon compounds. The successful and extensive use of organosilicon reagents in organic synthesis can be interpreted in terms of the fundamental physical properties of silicon namely: electronegativity, bond strength to other elements, hyperconjugation and the participation or lack of involvement of its valence p and empty d-orbitals. Silicon occupies a position below carbon in group IVA of the Periodic Table. Its electronic configuration, $3s^2 3p^2$, indicates quadrivalence but several aspects of its bonding to other elements differ from those of carbon. Silicon, because of its position in the Periodic Table is more electropositive than carbon, for instance on the Pauling scale, the values are : silicon 1.8, carbon 2.5 and hydrogen 2.1. The electronegativity of hydrogen is intermediate between that of silicon and carbon. This suggests that the silicon - carbon bond, is polarized and cleaves in the direction of Si^+C^- , either via nucleophilic attack at silicon or electrophilic attack at carbon. Further, the Si-C bond is more polarised than the H - C bond¹⁸ and therefore organosilicon compounds are expected to be more

reactive than the corresponding hydrocarbons. Indeed, it has been shown that when a C - H bond is cleaved by a particular reagent, the corresponding C-SiMe₃ can be similarly, but more readily cleaved.

Compared with their carbon analogues, silicon forms stronger single bonds with electronegative elements (oxygen, nitrogen, halogen), but weaker ones with carbon and hydrogen. A comparison of the average bond energies in kJ mol⁻¹ between carbon and silicon with various elements is summarised in Table 1.1.

Table 1.1 Average bond energies (kJ / mol)¹⁹

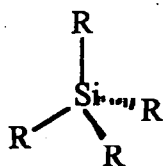
Element (X)	C	Si
H	413	320
C	345	306
N	304	365
O	357	463
F	485	594
Cl	339	406
Br	284	316
I	219	234

The relative inertness of the Si-F bond to hydrolysis reflects the fact that it is one of the strongest single bonds known. Partial double bond character, as a consequence of p π -d π bonding is believed to be responsible for the considerable strengths of the Si - X bond²⁰. The reactivity of the Si-X group towards nucleophilic reagents has been correlated with their ionic bond energies²¹ (Table 1.2).

Table 1.2 Ionic bond energies (kJ / mol)

	C	H	O	F	Cl	Br	I
Si	914	1044	1093	992	795	748	700

The ionic bond energy is defined as the sum of the energy required to place a positive charge on silicon (ionisation potential) and a negative charge on X (electron affinity). The ionic bond energies generally agree with the trend of reactivities of the various bond types e.g., $\text{Si-I} > \text{Si-Br} > \text{Si-Cl} > \text{Si-O} > \text{Si-H} > \text{Si-C}$. Despite this correlation, it is also proposed that the reactivity of organosilicon compounds stems from the ability of silicon to form 5 co-ordinate intermediates. Most organosilanes have a tetrahedral arrangement about silicon, which is consistent with the presence of sp^3 -hybridised orbitals on silicon (Figure 1).

**Figure 1**

However, in contrast to carbon, numerous compounds are known in which silicon has expanded its co-ordination shell to accommodate more than four ligands^{22, 23, 24}. A few examples of hypervalent silicon compounds are shown in Figure 2.

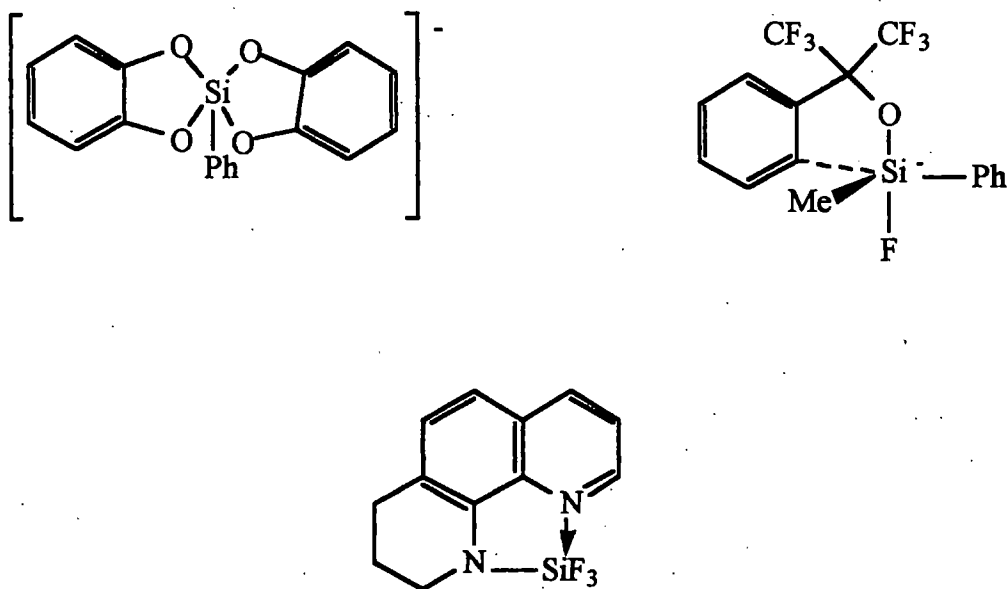
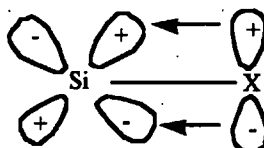


Figure 2

The formation of higher co-ordinate silicon is often attributed to the low - lying vacant d-orbitals on silicon which are not readily available on carbon. These low-lying orbitals can participate in (p-d) π bonding as shown in Figure 3. In this way, the lone pairs on the p orbitals of X overlap with the empty 3d orbitals of the adjacent silicon through a donor-acceptor type interaction.

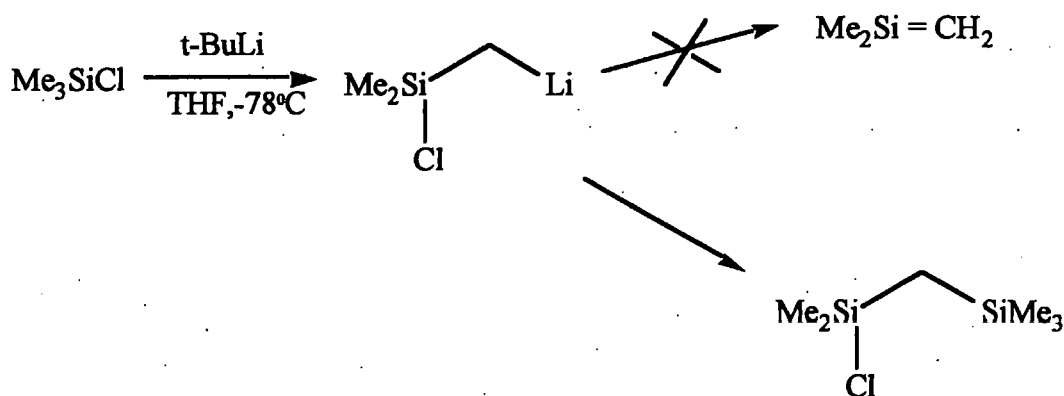


p π - d π bonding

Figure 3

These low-lying d-orbitals are said to account for some of the reactions of organosilicon compounds²⁵. An anion α to silicon is stabilised by (p-d) π bonding between the filled p-orbital on the carbon and the vacant d-orbital on the silicon⁸. This is sufficiently strong to stabilise many α -silyl carbanions. Generally though, these carbanions are further stabilised

by adjacent electron - withdrawing substituents. A striking demonstration of this observation and of the difficulty of forming Si=C double bonds is provided by the reaction shown in Scheme 1.2. A carbon-lithium bond is formed adjacent to the silicon atom, yet elimination of the chloride does not take place; instead silylation produces a new C-Si bond²⁶.



Scheme 1.2

There are no conformational requirements in the (p-d) π bonding model. The degree of (p-d) π overlap is constant, regardless of rotation about the Si-X bond, as a consequence of the symmetry of the five 3d-orbitals on silicon.

1.1.2 Directive effects of the silyl group

In organic syntheses using silicon compounds, one of the most important activating and directing effects is the stabilization of β -silylcarbonium ions, (β -effect). Two explanations have been proposed for this effect; hyperconjugation and a bridging mechanism. The hyperconjugation explanation involves overlap with the Si-C σ bond, giving (p- σ) π conjugation. The proposed involvement of the Si-C linkage can be understood if one recognises the high degree of polarization of the Si-C bond as a result of silicon being more electropositive than carbon. Hence the occupied p-type orbitals that make up the Si-

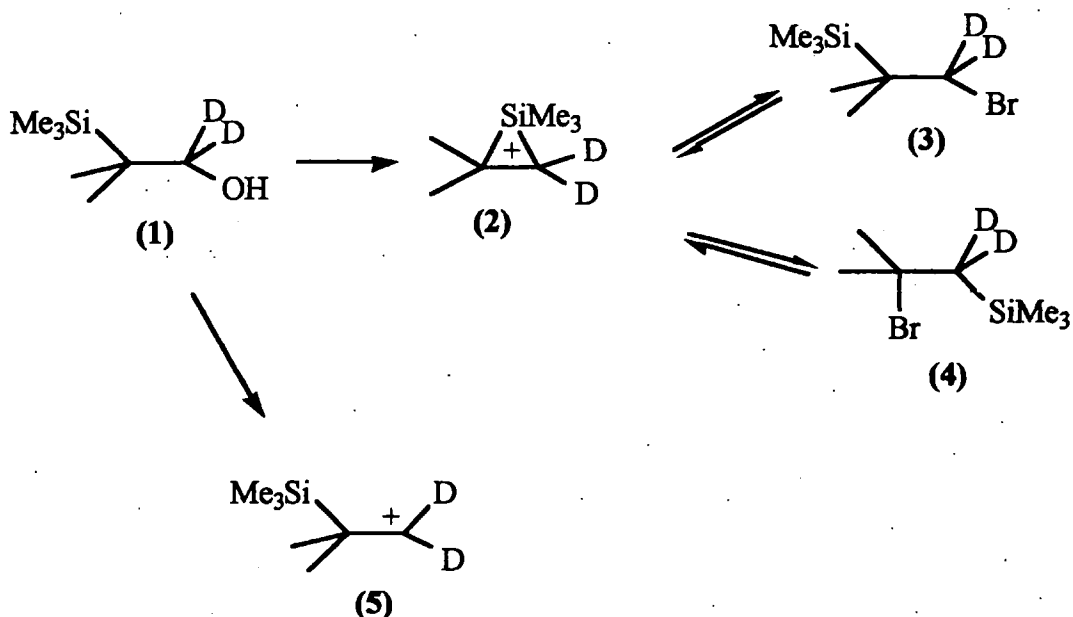
C bond have higher coefficients on carbon than on silicon. Consequently, the Si-C bond has greater ability to stabilize an adjacent electron-poor centre by orbital overlap (Figure 4).



Figure 4

The overlap of these filled orbitals with an empty p-orbital (hyperconjugation²⁷) lowers the energy more than the corresponding overlap from an H-C or C-C bond. For hyperconjugation to be at a maximum the Si-C bond must be coplanar with the p orbital with which it is interacting²⁸.

The alternative explanation (bridging mechanism) for the stabilization of a β -carbonium ion by the trimethylsilyl group has been reported independently by Eaborn²⁹ and Jarvie³⁰. This mechanism involves the interaction of silicon by internal neighbouring group participation, to form a three-membered ring siliconium ion. A further study³¹ found that the reaction of a dideuterio- β -hydroxysilane **1** with phosphorus (III) bromide gave a directly substituted bromide **3** together with a rearranged bromide **4** in equal amounts (Scheme 1.3). These results which supported the cyclic siliconium intermediate were interpreted in terms of anchimeric assistance by the trimethylsilyl group, to give a bridged intermediate **2**.



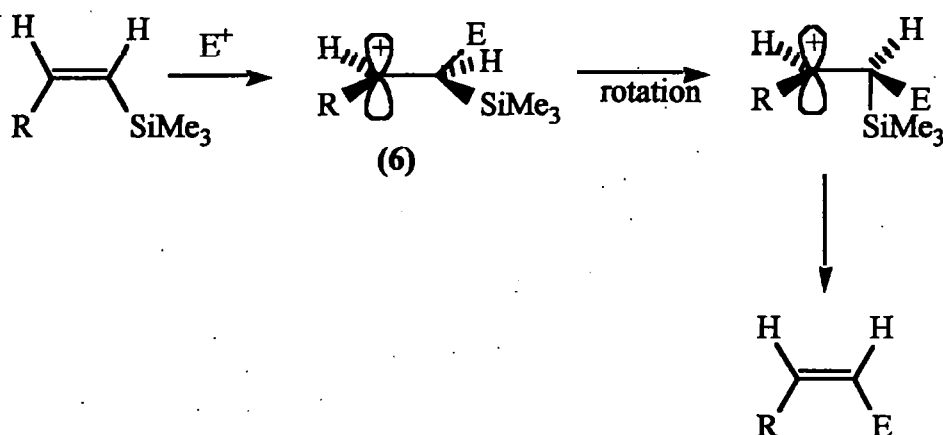
Scheme 1.3

A possible alternative explanation is that the open-chain, hyperconjugatively stabilised carbonium ion, **5** is formed, but rapidly undergoes facile 1, 2 silyl migration¹² before being trapped by the bromide ion. From calculations by Jorgensen³² on primary systems assessing the size of the β -effect, the cyclic form had a higher stabilisation energy compared to the orthogonal opened form.

1.2 The chemistry of vinylsilanes

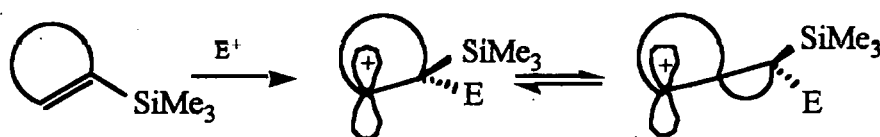
The ability of the trialkylsilyl group to influence the regio- and stereospecificity of a variety of transformations of vinylsilanes has given rise to considerable interest in methods of preparing such compounds with specific substitution patterns and stereochemistry. These vinylsilanes have found very extensive use in organic synthesis, where they are used as precursors to many classes of compounds³³. The addition of an electrophile to a vinylsilane results in the build-up of positive charge β -to the silicon (Scheme 1.4). Such a

species is stabilised by hyperconjugation. The addition of the electrophile has the geometrical requirement that the positive charge on the β -position, can only be stabilized if it is contained in a $2p_z$ orbital that is in the same plane as the C-Si σ -bond.



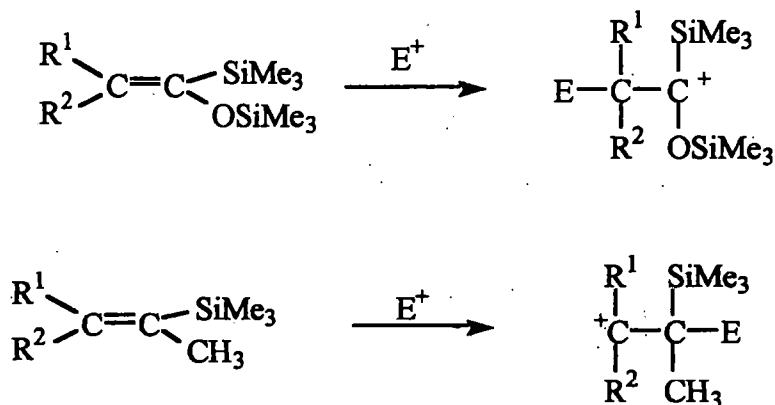
Scheme 1.4

This geometric condition can impose severe limitations upon the use of the β -effect to stabilize electrophilic additions to vinylsilanes. In acyclic systems, there is usually no problems. As the incoming electrophile approaches the vinylsilane to give the intermediate 6, rotation about the central carbon-carbon bond can take place to bring the vacant p -orbital into the same plane as the carbon - silicon bond. However, for cyclic vinylsilanes, particularly in conformationally rigid systems, it may be difficult, and in certain cases, impossible for the carbon-silicon bond to move into the same plane as the vacant $2p_z$ orbital³⁴ (Scheme 1.5).



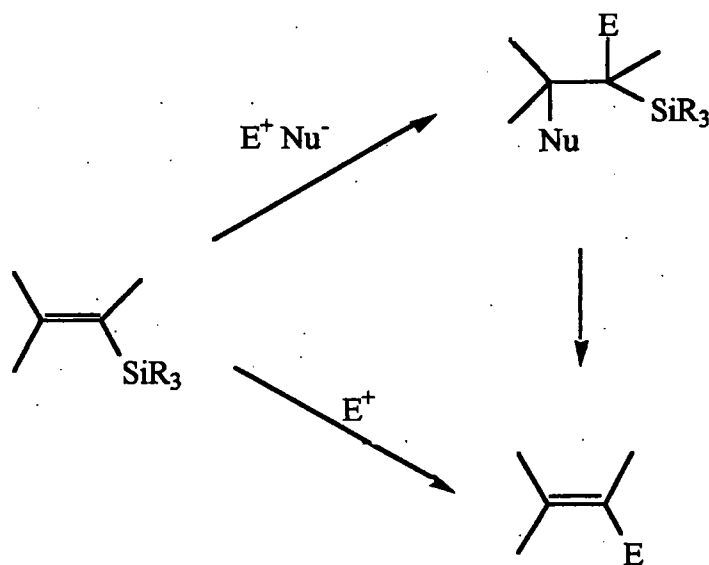
Scheme 1.5

Electrophilic additions to vinylsilanes are normally regioselective unless the α -carbon carries a substituent, such as a trimethylsiloxy group or a phenyl group, which can stabilise the α -carbonium ion more effectively than silicon can stabilise the development of a β -carbonium ion^{35,36} (Scheme 1.6).



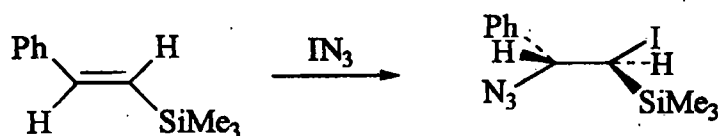
Scheme 1.6

Vinylsilanes react readily with a variety of electrophiles with either addition to the double bond or substitution of the R_3Si group, as shown in Scheme 1.7. The addition product often undergoes subsequent elimination to give overall substitution.



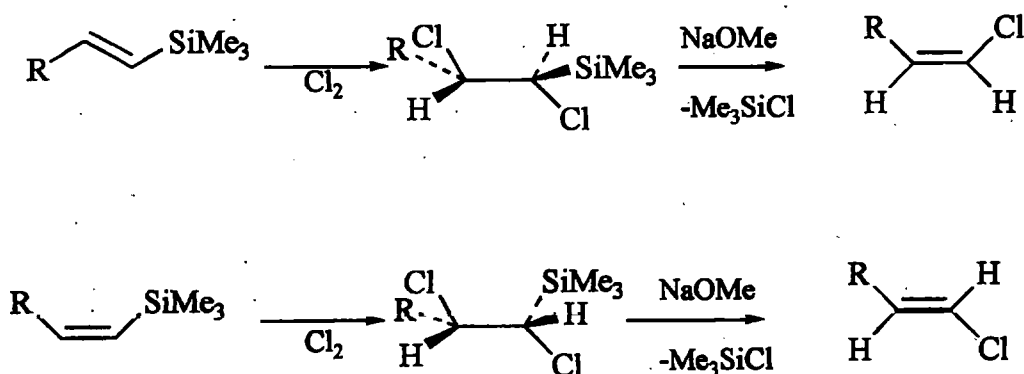
Scheme 1.7

The stereochemical outcome of substitution, retention or inversion, depends on the electrophile together with the reaction conditions. The stereospecific nature of the reaction was first demonstrated by Koenig and Weber, who showed that (*Z*)- and (*E*)- β -trimethylsilylstyrenes were converted to (*Z*)- and (*E*)- β -deuteratedstyrenes by deuterium chloride or bromide with complete retention of stereochemistry³⁷. Miller³⁸ has shown that unhindered 2-alkylvinylsilanes can be converted regio- and stereoselectively into the corresponding vinyl chloride with net inversion of configuration. Trialkylsilanes, like most alkenes undergo *anti*-addition especially if halonium ions are involved³⁹ (Scheme 1.8).



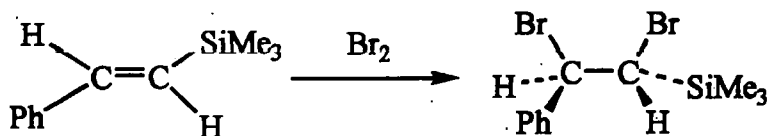
Scheme 1.8

The products of inversion are observed if this *anti*-addition is followed by an *anti*-elimination (Scheme 1.9).



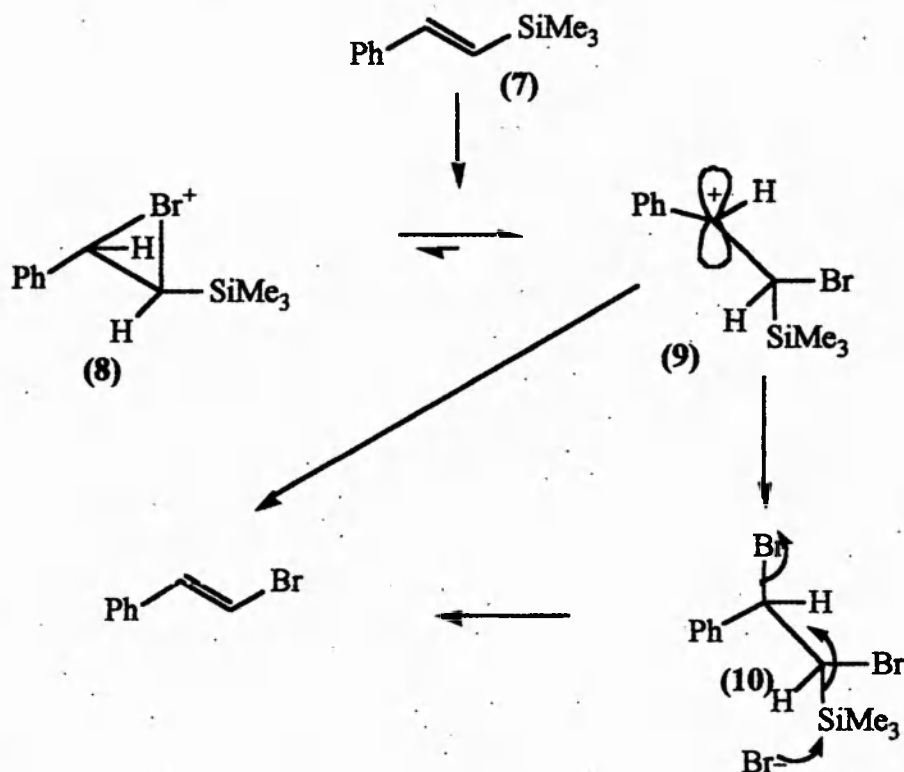
Scheme 1.9

However, *syn*- addition has been observed in some cases, as in the bromination of β -silyl - styrenes. Weber and Brook^{40, 41} showed that whilst the reaction took place by an addition - elimination pathway, it led to retention of stereochemistry (Scheme 1.10).



Scheme 1.10

The proposed mechanism, which involves *syn*-addition followed by *anti*- elimination, is shown in Scheme 1.11. A possible explanation for this *syn*- addition is that the phenyl group promotes open chain carbonium ion formation. In this case conformation **9** has maximum hyperconjugative stabilization, and is formed by the least motion rotation about the carbon-carbon bond. Attack of the bromide ion then occurs from the less hindered side, *anti*-to the β -silyl group giving the overall *syn* - addition product **10**. Alternatively, the carbocation **9**, could undergo desilylation to give retention via direct substitution without going through **10**.

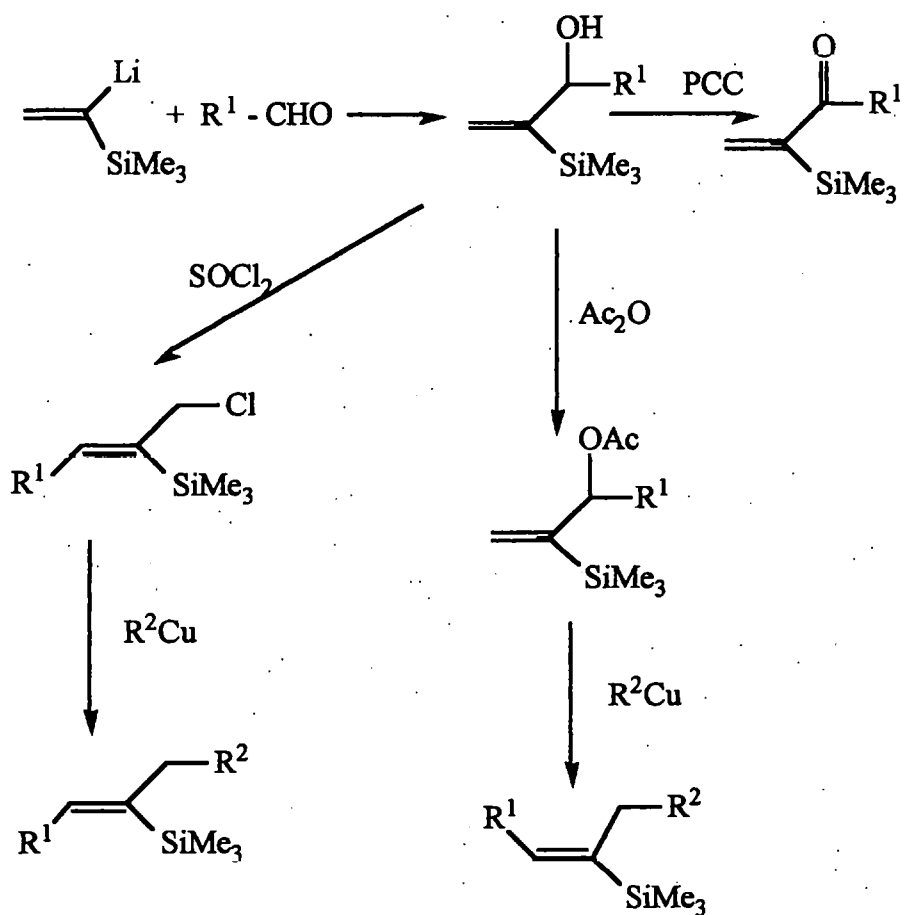


Scheme 1.11

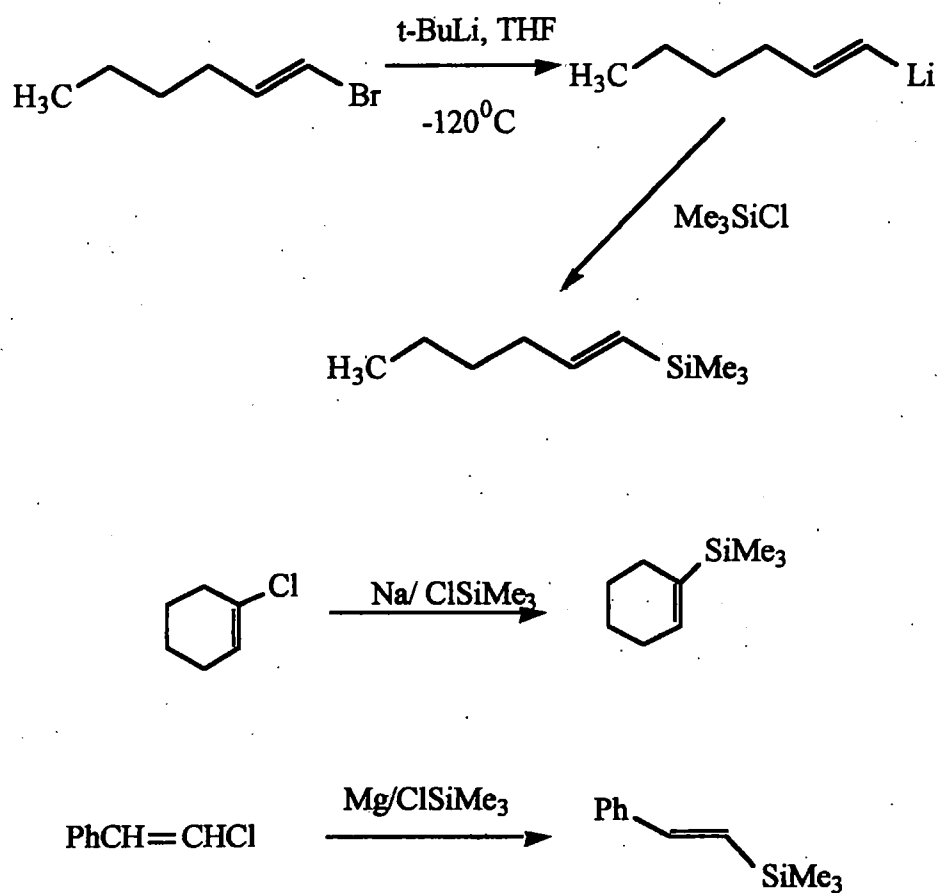
1.2.1 Synthesis of vinylsilanes

As a result of their rich chemistry and the fact that vinylsilanes are used as precursors to many classes of compounds, many routes have been devised for the preparation of substituted and unsubstituted vinylsilanes. Some of the recent methods from acetylenes, carbonyl compounds and vinyl halides are summarised in the Schemes 1.12⁴², 1.13⁴³ and 1.14⁴⁴ respectively.





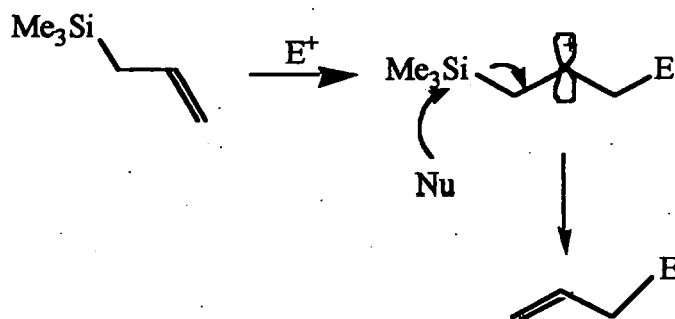
Scheme 1.13 Synthesis of Vinylsilanes from carbonyl compounds.



Scheme 1.14 Synthesis of vinylsilanes from vinylhalides

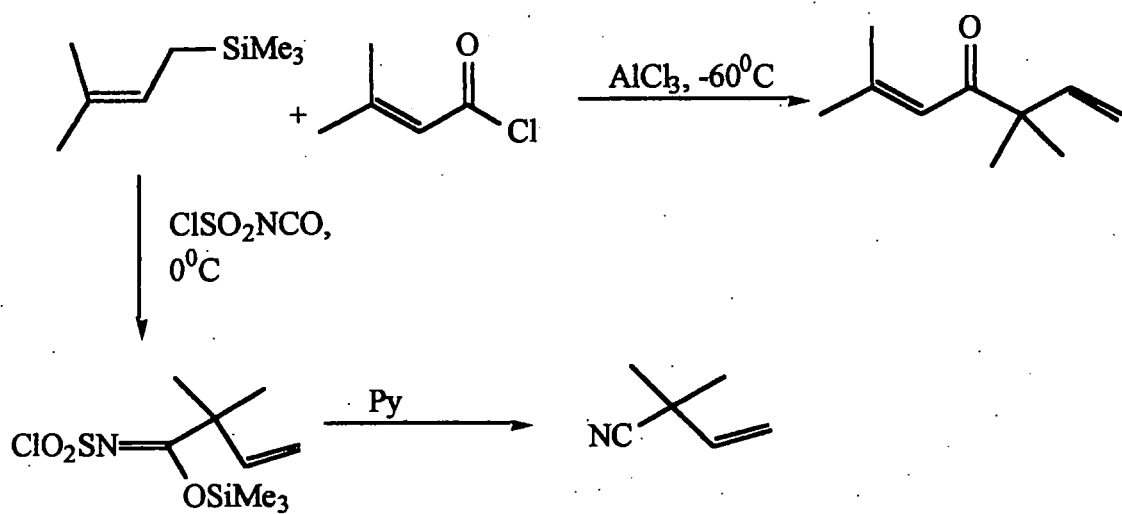
1.3 The chemistry of allylsilanes

Although the structure of allylsilanes and their reactivity profile was reported more than 40 years ago, by Sommer⁴⁵, the real potential of these compounds was realised around the mid 1970s as a result of the pioneering work of Calas⁴⁶, Corriu⁴⁷ and Fleming⁴⁸. Allylsilanes are relatively stable compared to other allylmetal species. They react with electrophiles in the manner shown in Scheme 1.15.

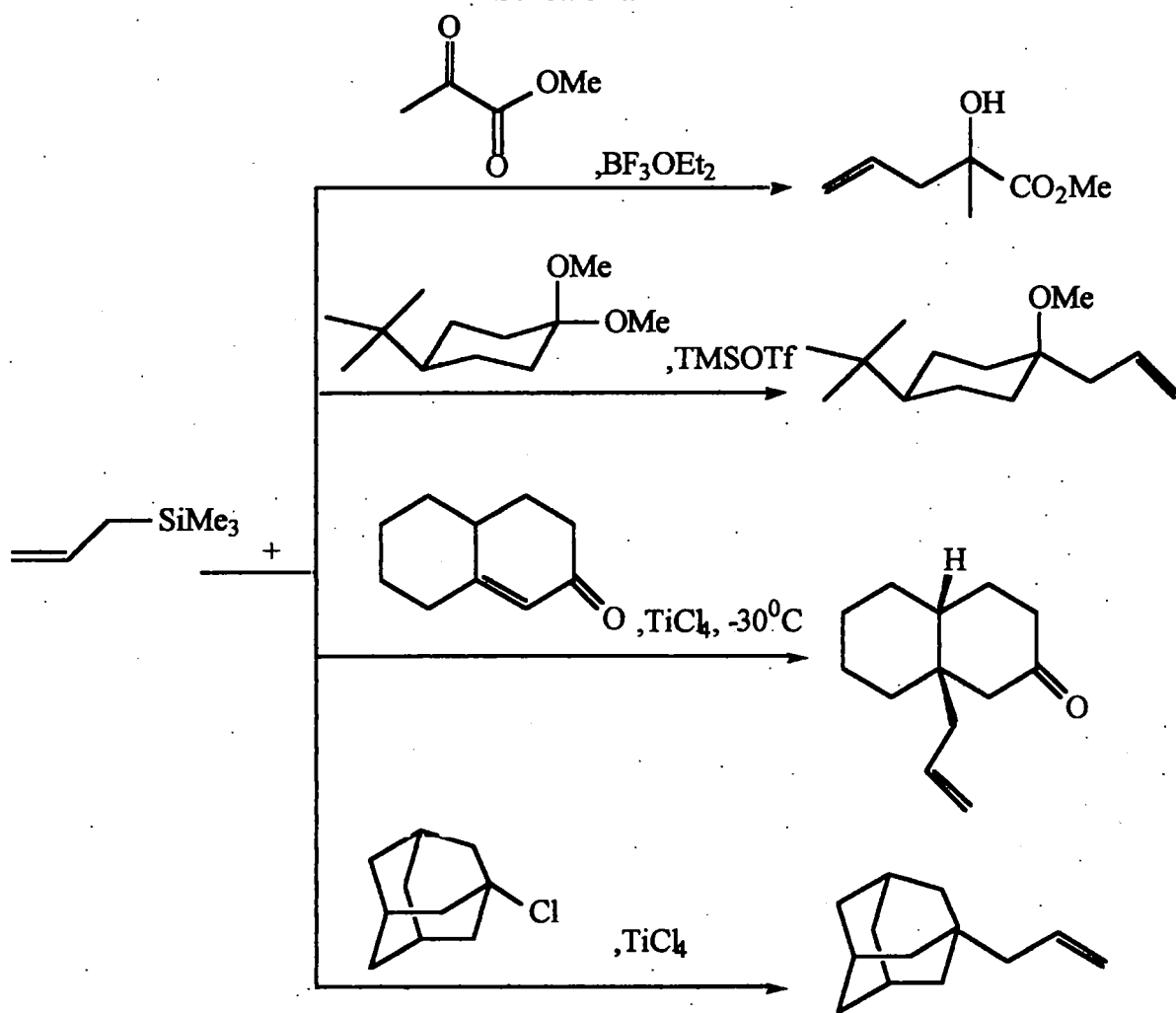


Scheme 1.15

Attack at the C-3 of the allyl system generates a cation stabilised by the neighbouring C-Si bond. This is followed by the displacement of the silicon by a nucleophile. The C-Si bond should be in the same plane as the empty p-orbital in order to stabilize the positive charge. From a purely synthetic point of view, the most important feature of allylsilane chemistry is that the electrophile enters on the terminus of the allyl system, and the π -system is relocated adjacent to the original position of the silicon. As a result of this predictability, and the high nucleophilicity of allylsilanes, they have found many uses in synthesis, some of which are shown in Schemes 1.16^{49,50} and 1.17^{51,52}.

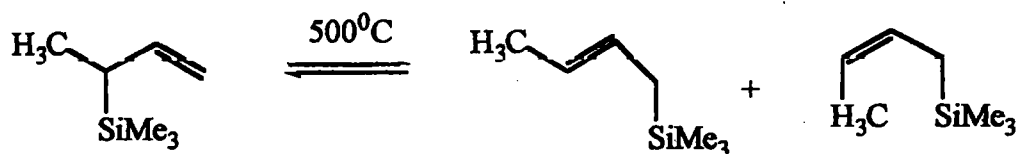


Scheme 1.16



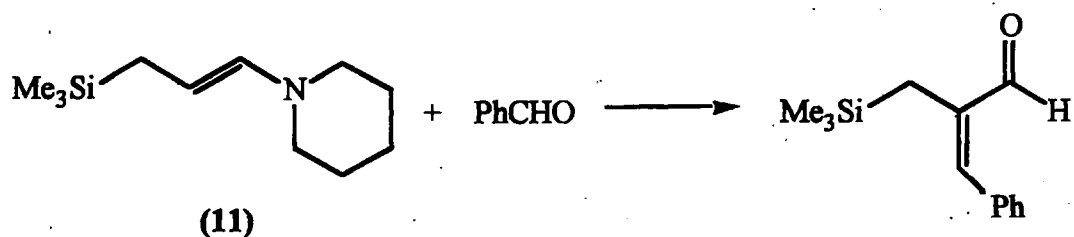
Scheme 1.17

The reaction of allylsilanes with electrophiles is usually regioselective, giving a single product, this is because, unlike other allylmetals, allylsilanes rearrange only at high temperatures⁵³ (Scheme 1.18).



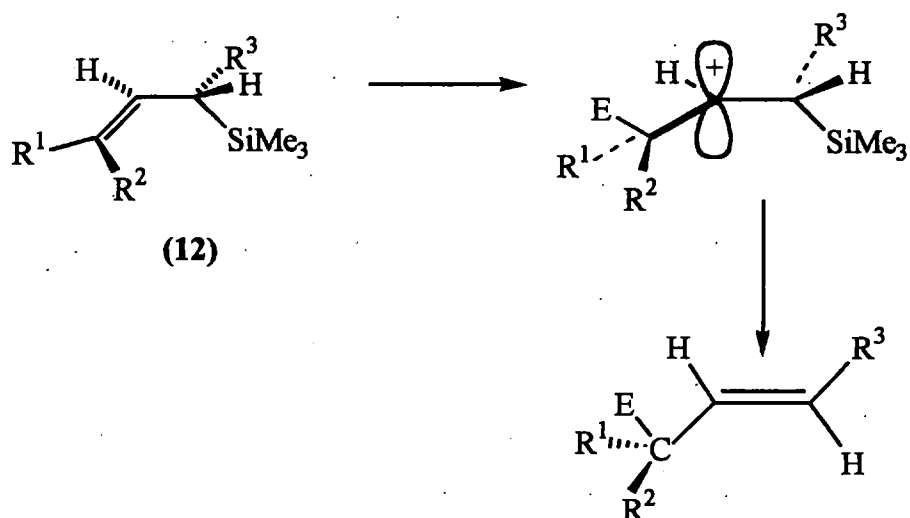
Scheme 1.18

The silicon directing effect is not observed if the molecule contains a substituent that can stabilize the cationic intermediate to a larger extent than the silicon. For example, compound **11** which is both an allylsilane and an enamine behaves only as an enamine⁵⁴ (Scheme 1.19).



Scheme 1.19

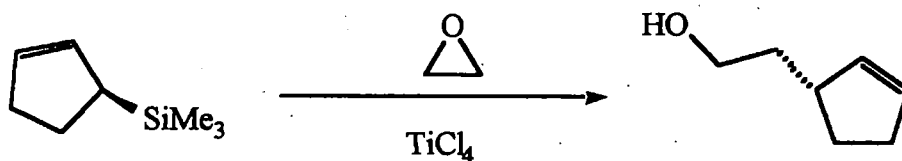
In reactions involving allylsilanes, the most stable conformation of the starting material is **12** as depicted in Scheme 1.20, with the carbon-silicon bond overlapping with the π -lobes of the carbon-carbon double bond. In this conformation, the bulky R^3 group is located as far away from the double bond as possible to minimise steric repulsion.



Scheme 1.20

This preferred ground state controls the stereochemical outcome of electrophilic reactions. The electrophile attacks the preferred conformation from the side opposite to the trimethylsilyl group (*anti* - attack), to form a cationic intermediate. The subsequent displacement of the silyl group thus gives an alkene with a specific stereochemistry. This *anti* stereoselectivity has been confirmed principally through the work of Eschenmoser⁵⁵ Kumada⁵⁶, Kitching⁵⁷ and Fleming⁵⁸.

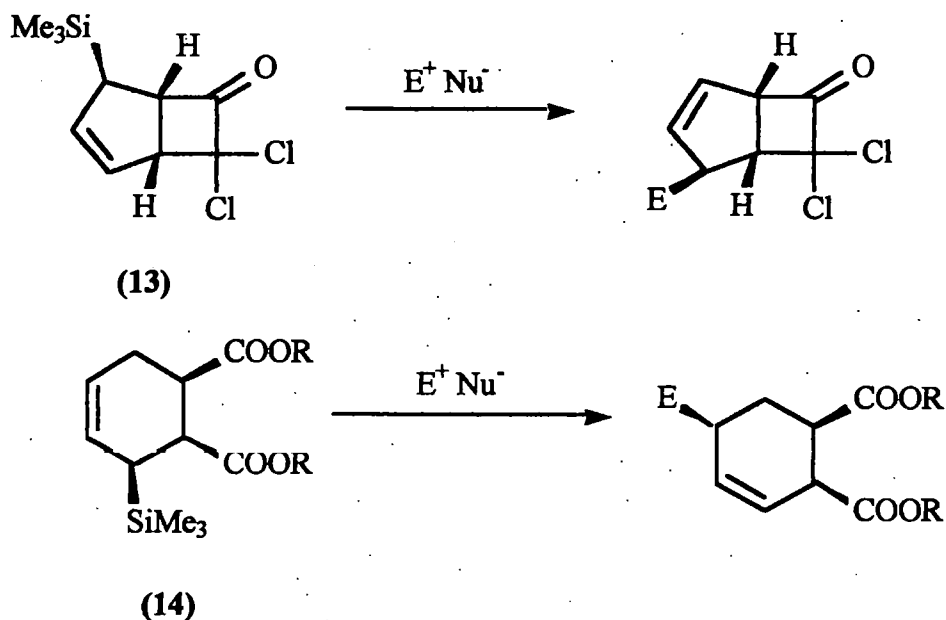
Kumada has shown that cyclic allylsilanes, free from any stereochemical bias, give predominantly *anti*-addition⁵⁹ (Scheme 1.21).



Scheme 1.21

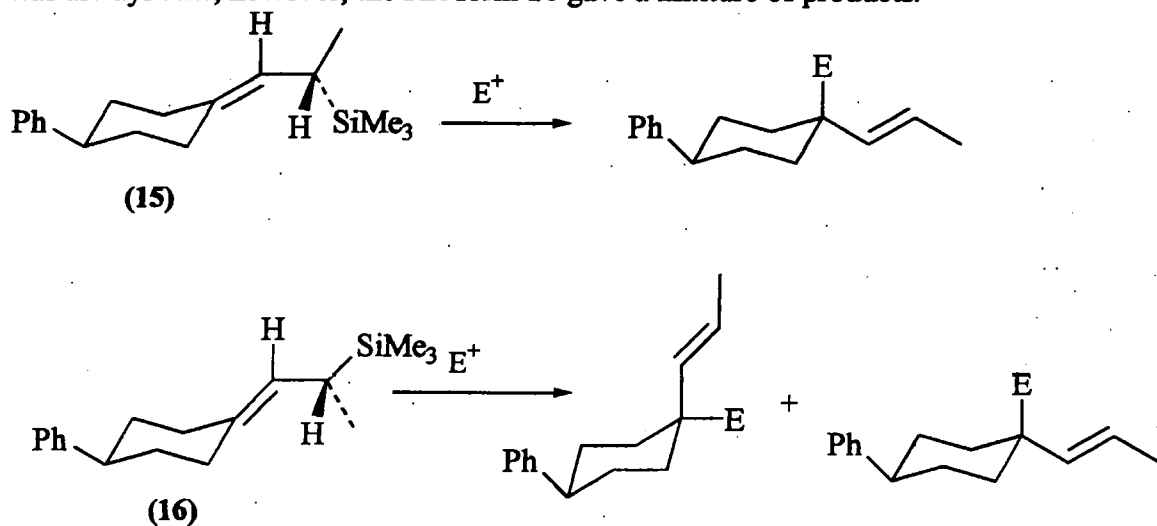
Despite the general preference for *anti*-selectivity, other stereochemical features of the allylic system may dominate. In the cyclopentenyl system 13, electrophilic substitution

occurred with *syn* - selectivity⁶⁰. The electrophile only attacks the *exo*-face, resulting in retention of configuration. However, in the cyclohexenyl system 14, electrophilic attack occurred with *anti* - selectivity⁶¹ (Scheme 1.22).



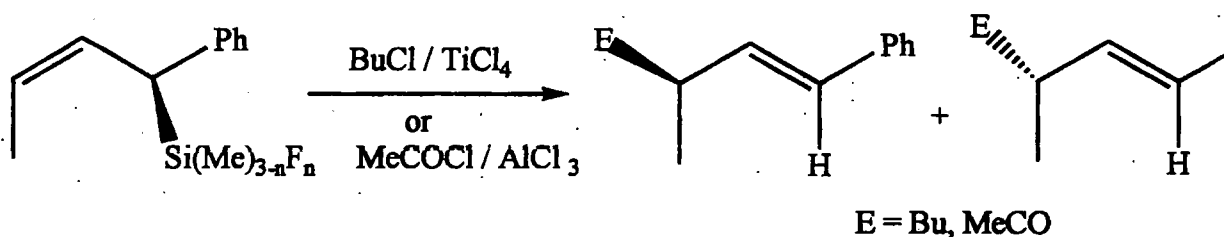
Scheme 1.22

The influence of structure on the stereochemical outcome has also been demonstrated by Fleming⁶² (Scheme 1.23). With the *RS* form 15, the addition of the electrophile (e.g. H^+) was always *anti*, however, the *RR* form 16 gave a mixture of products.



Scheme 1.23

Deuteriodesilylation of the RR form **16** indicated that the *syn* addition occurred via an indirect pathway, whereas *anti* - addition occurred as expected. It was concluded that the cyclohexyl ring had a preference for axial protonation and when this axial preference opposes the *anti* selectivity of the allylsilane, the molecule finds another pathway. Recent work⁶³ has shown that the presence of fluorine substituents on silicon reduces the stereoselectivity of substitution (Scheme 1.24). With $n=1$ the reaction proceeded in an *anti* - fashion, showing that the σ - π conjugation of the C-Si bond with the olefin π -system is still pronounced.

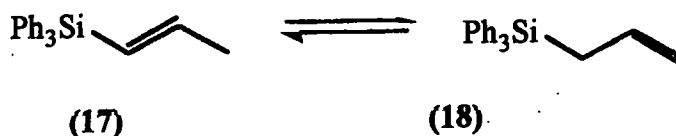


Scheme 1.24

With $n=2$, there was a distinct loss of enantiomeric purity indicating that σ - π conjugation is less important. With $n=3$, a poor yield of a racemic product was obtained. This decrease in σ - π conjugation is in agreement with the electronic nature of the fluorine substituent.

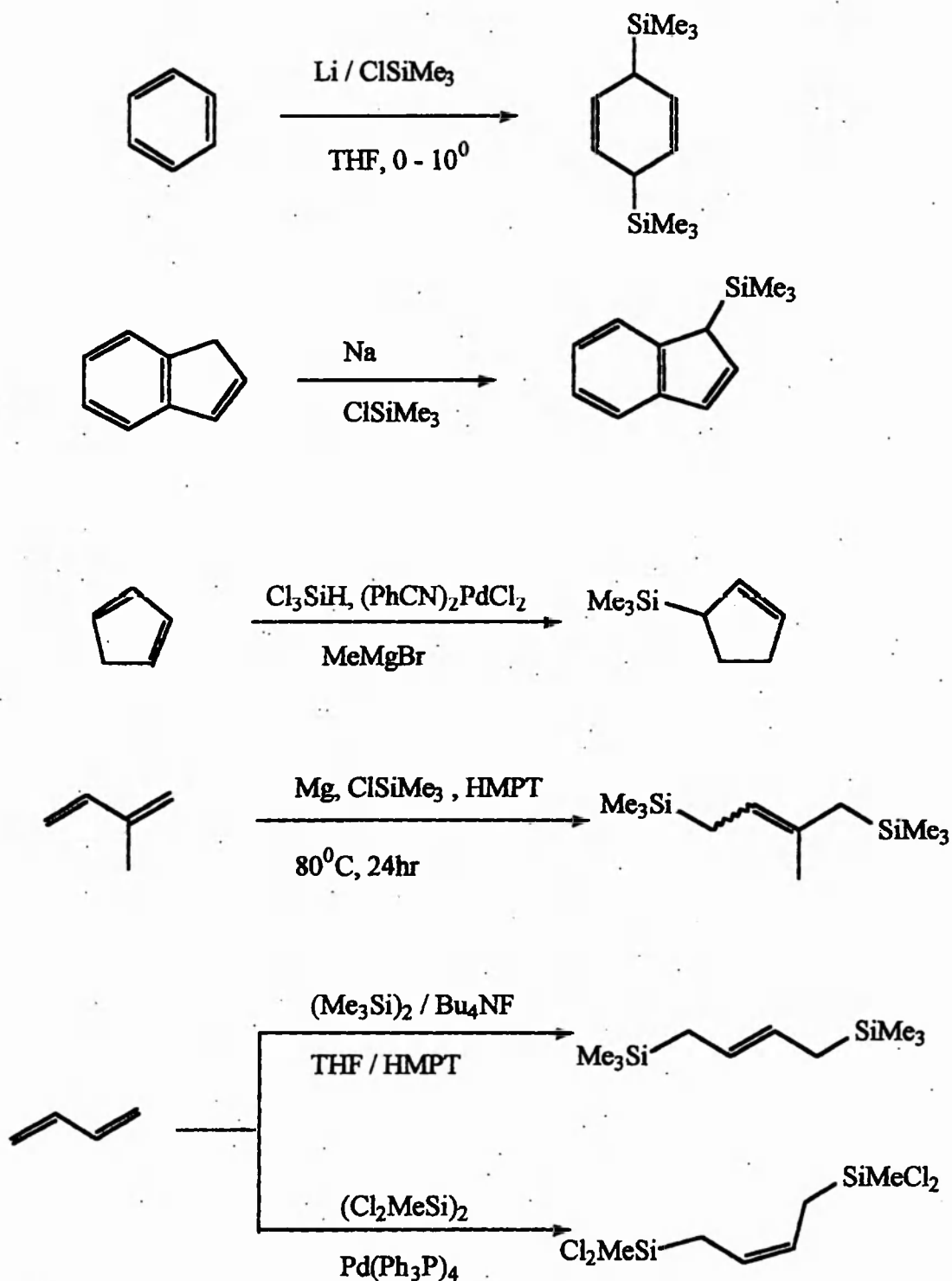
Allylsilanes are more reactive than vinylsilanes. Firstly, the hyperconjugative overlap of the C-Si bond of an allylsilane with the orbital of the π - bond will raise the energy of the HOMO and hence make the molecule reactive towards electrophiles. Furthermore, this overlap can stabilise the developing positive charge on C-2. This contrasts with the vinylsilanes where full hyperconjugative stabilization is only possible after rotation of the C-Si bond, through 90. Evidence in support of this proposal comes from the predominance of **17** under equilibrium conditions⁶⁴. Thus the ground state of **18** is higher in energy and since both have an identical intermediate for electrophilic attack by the proton the

activation energy for protodesilylation of allylsilane would be expected to be smaller than that for the vinylsilane 17.

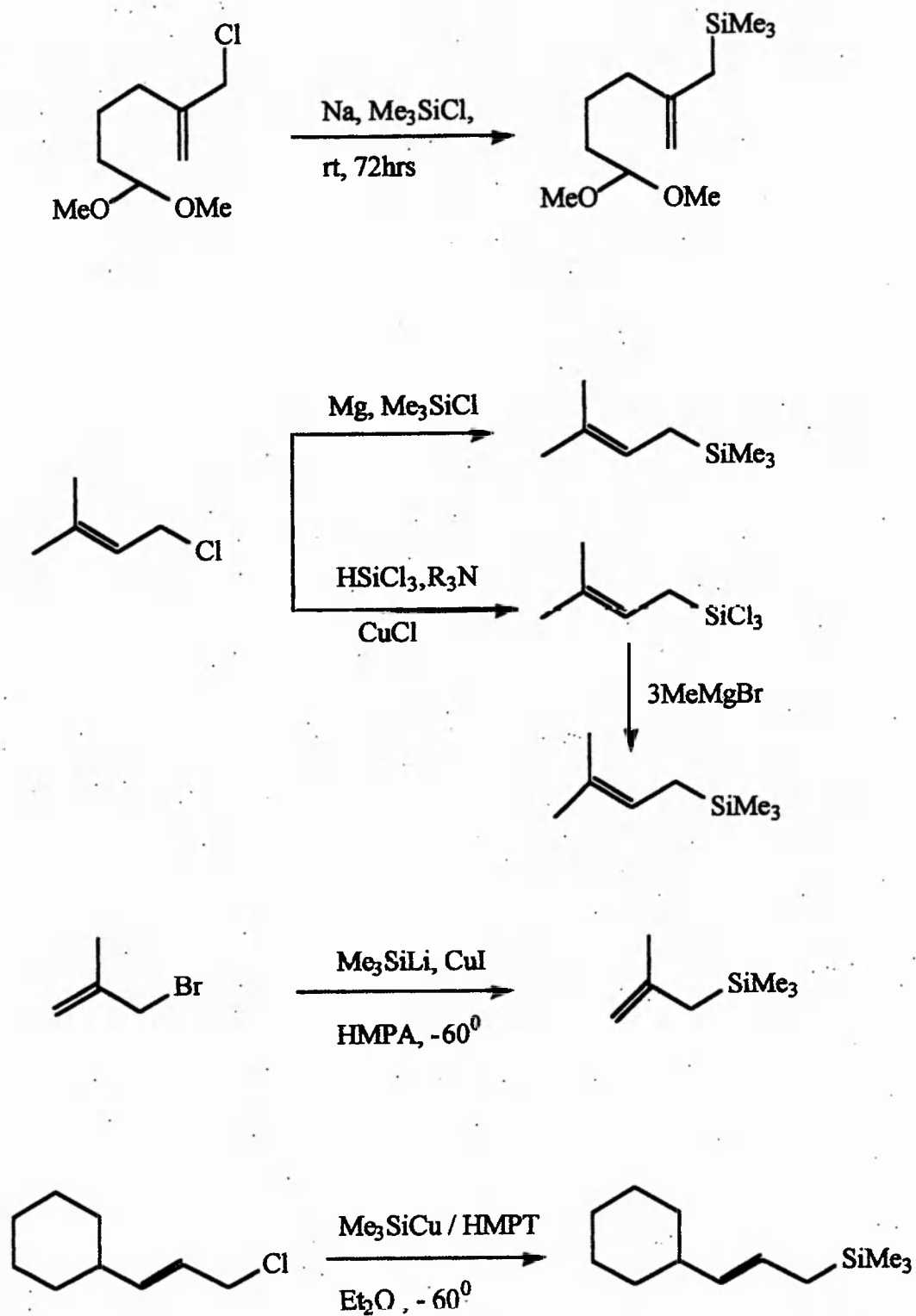


1.3.1 Synthesis of allylsilanes

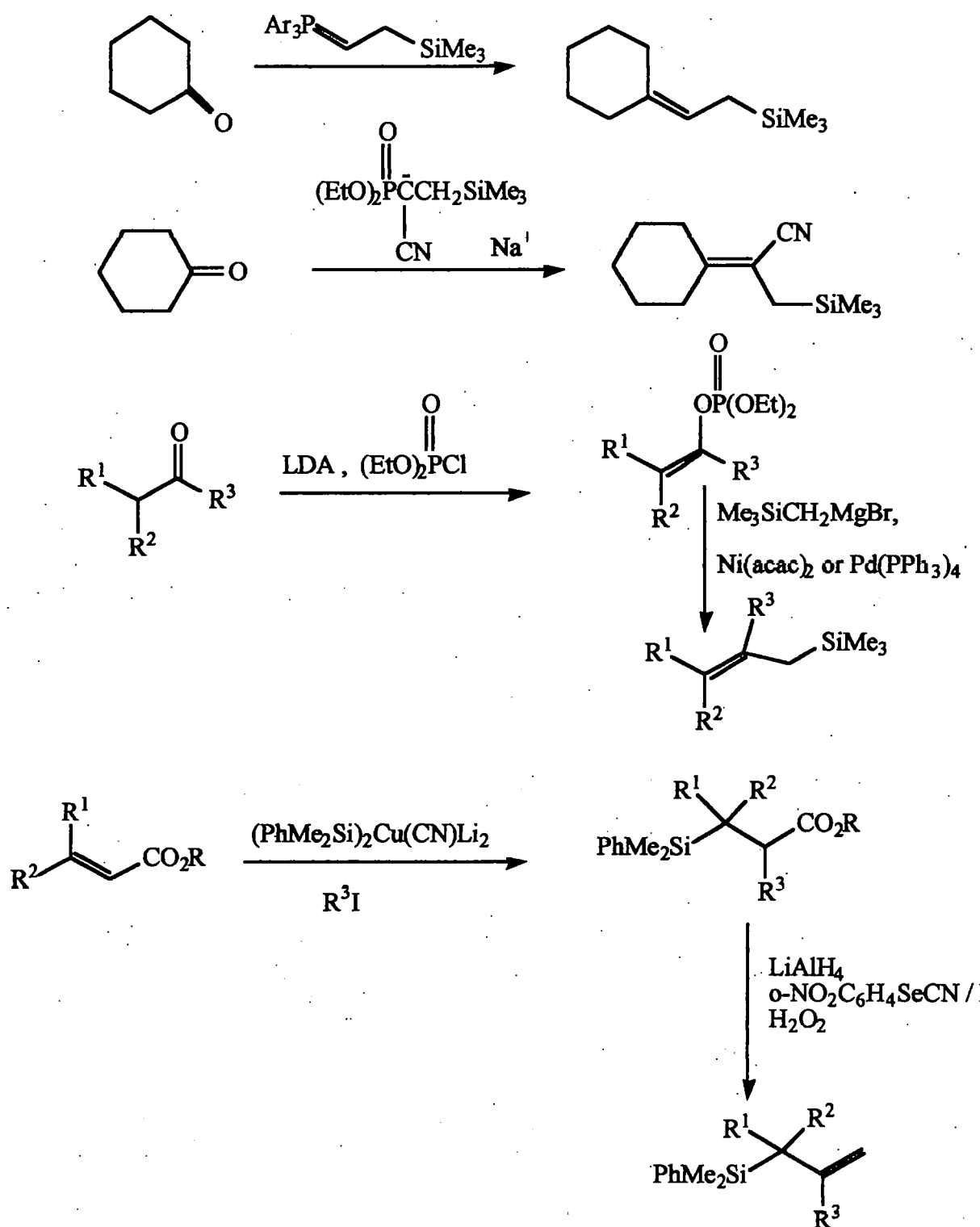
A number of methods have been developed for the synthesis of allylsilanes such as the silylation of allylmetal compounds⁶⁵. Calas has developed general methods of preparing allylsilanes. He has used reductive silylation⁶⁶ of aromatic compounds⁶⁷, dienes⁶⁸, allenes⁶⁹, allylic alcohols⁷⁰ and thioethers⁷¹. Carbonyl compounds can also be converted into allylsilanes⁷². A very good review article on the synthesis of allylsilanes has been published by Sarkar⁷³. Some examples of these methods are illustrated in the Schemes 1.25, 1.26, 1.27, 1.28 and 1.29.



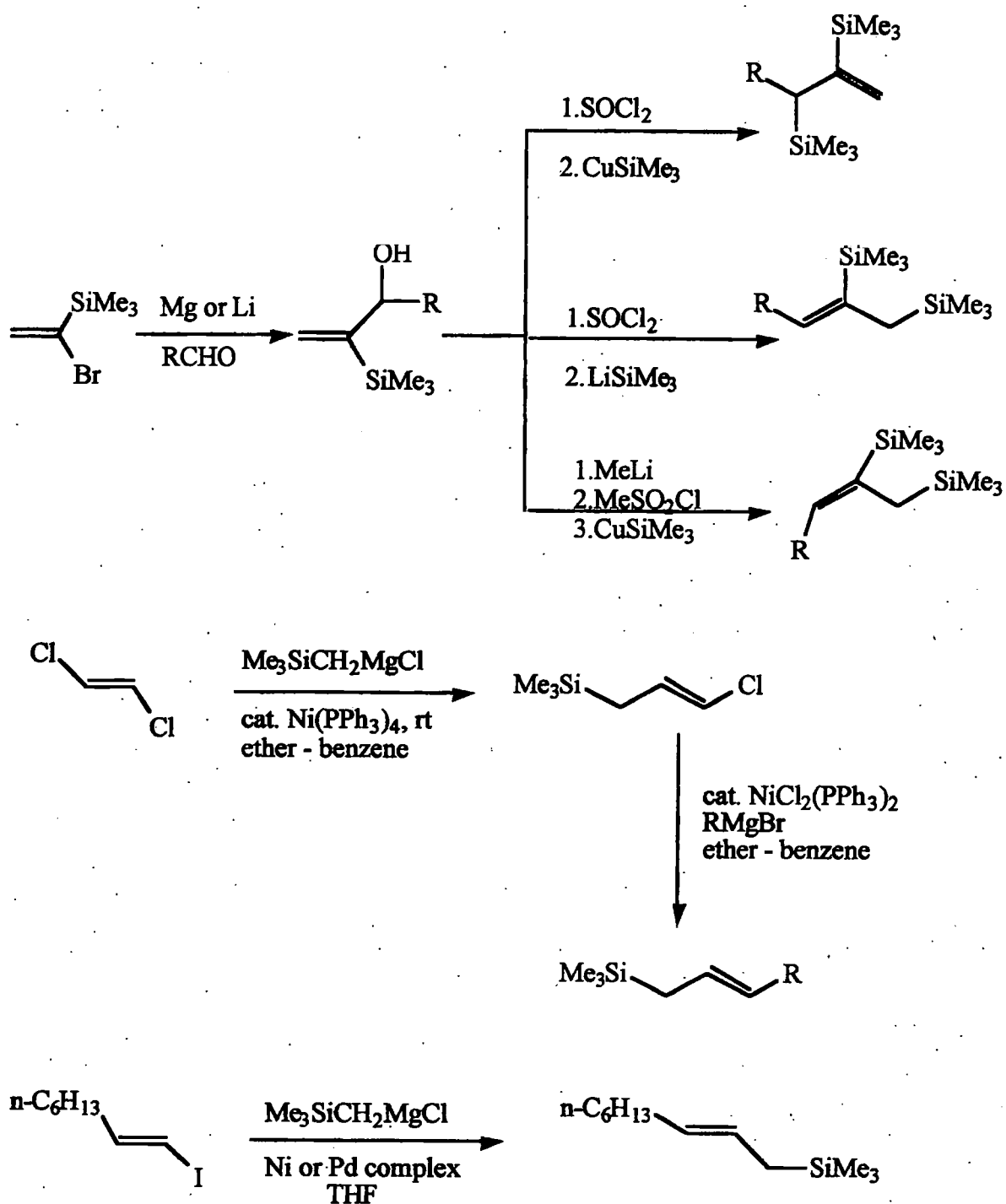
Scheme 1.25⁷⁴



Scheme 1.26 Synthesis of allylsilanes from allylic halides⁷⁵

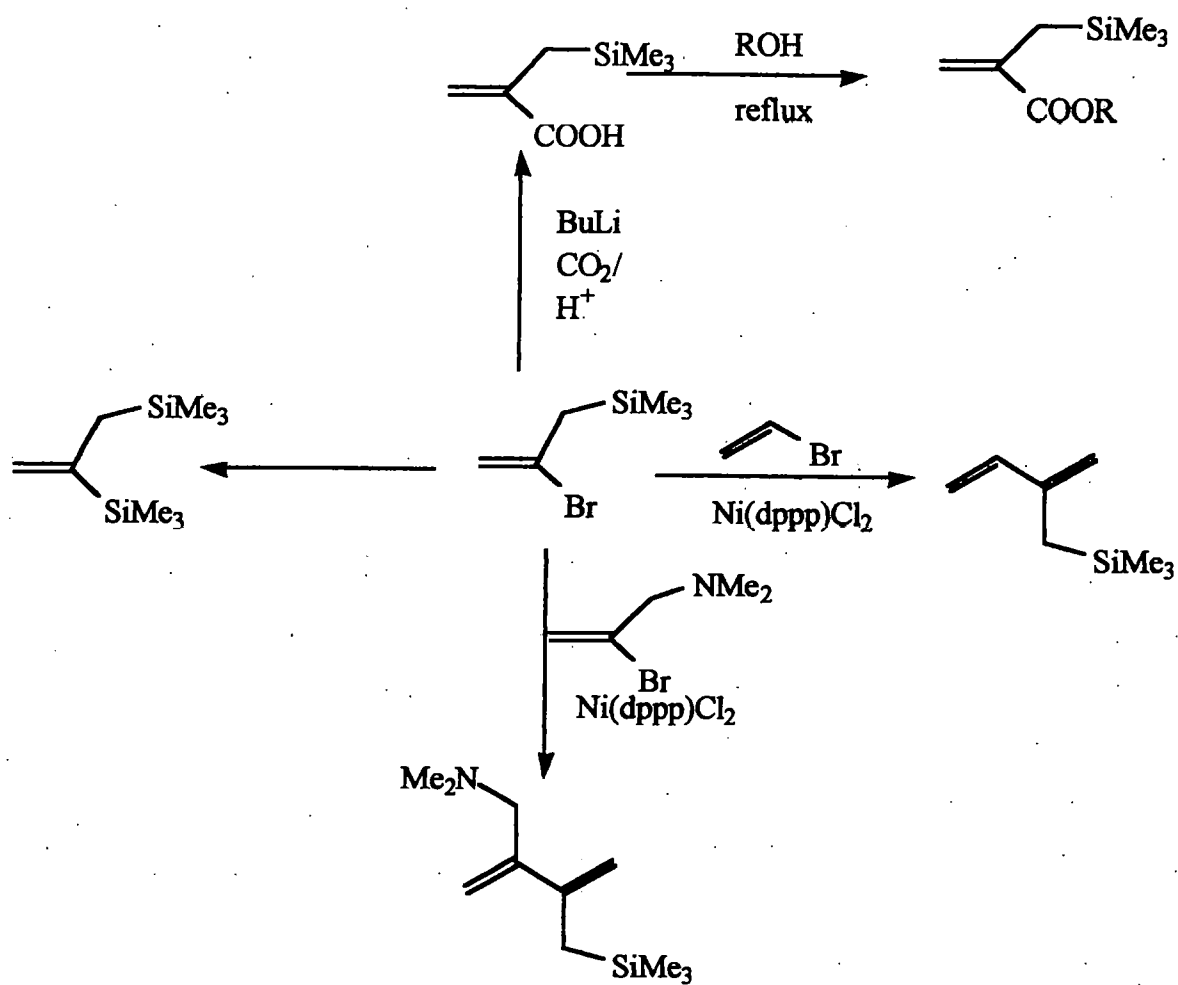


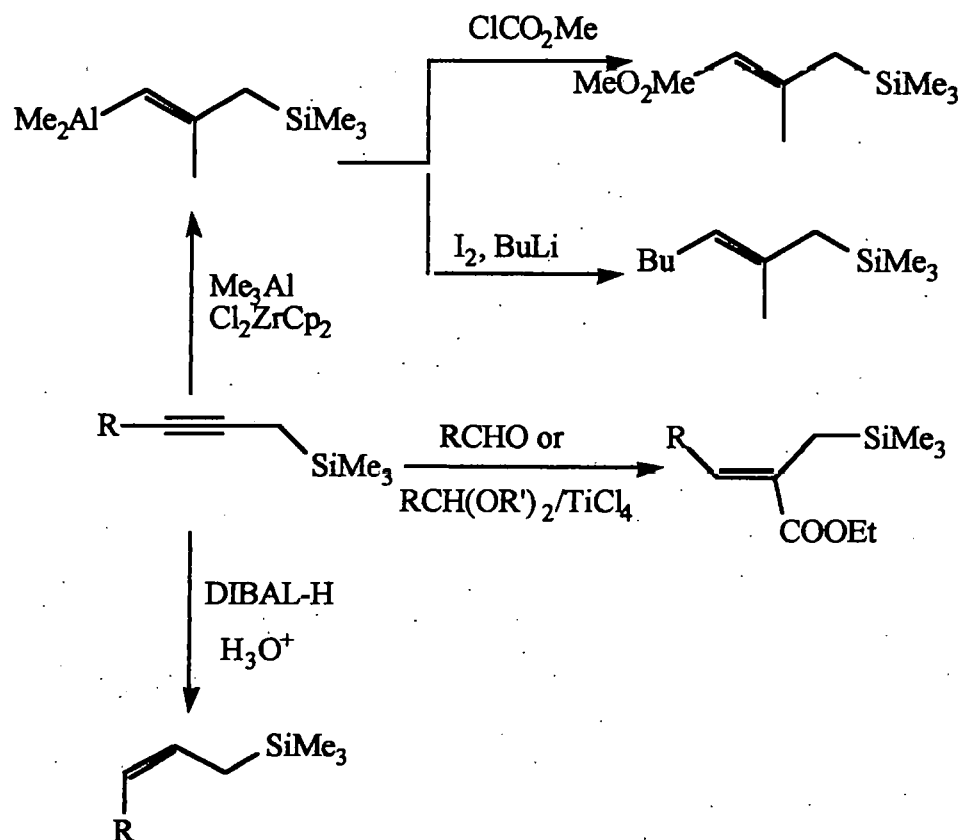
Scheme 1.27 Synthesis of allylsilanes from carbonyl compounds⁷⁶



Scheme 1.28 Synthesis of allylsilanes from vinyl halides⁷⁷

Scheme 1.28 continued:





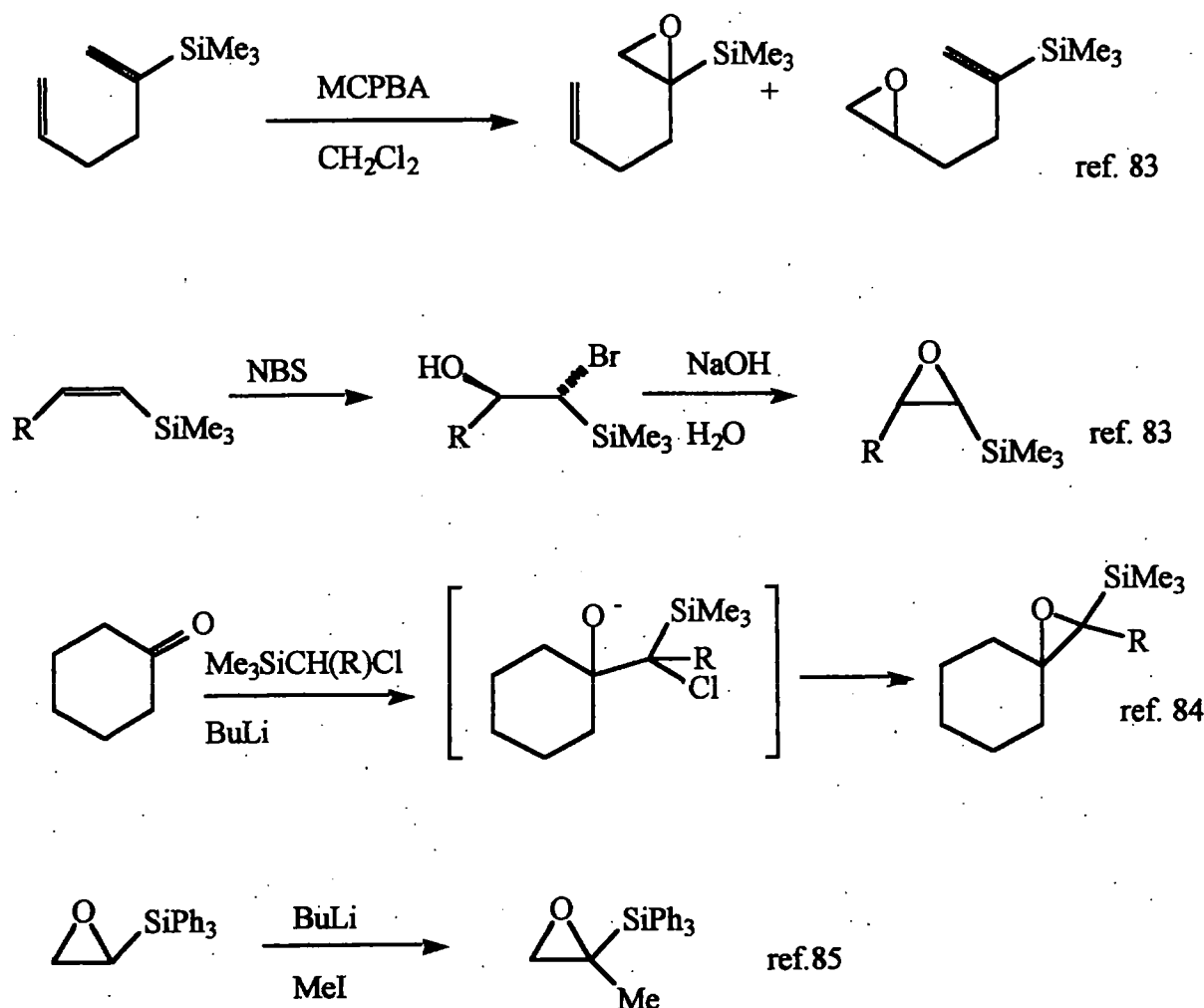
Scheme 1.29 Synthesis of allylsilanes from propargylsilanes⁷⁸

1.4 Silyl-substituted heterocycles

Heterocyclic compounds are very widely distributed in nature and are essential to life; they play a vital role in the metabolism of all living cells. There are a vast number of pharmacological active heterocyclic compounds, many of which are in regular clinical use. Some of these are natural products, for example antibiotics such as penicillin and cephalosporin and alkaloids such as morphine etc. However, the large majority are synthetic heterocycles which have found widespread use, for example as anti-cancer agent, pesticides, insecticides analgesics, dyestuffs and a host of others uses.

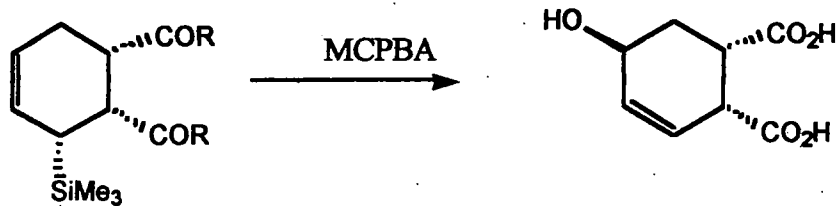
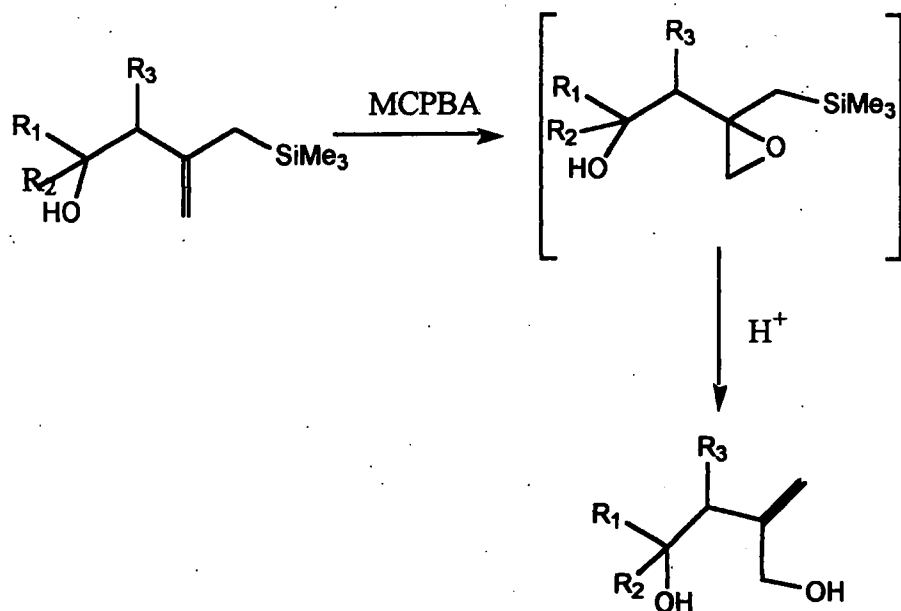
1.4.1 Synthesis of silylepoxydes

To date little synthetic use has been made of organosilicon compounds in heterocyclic chemistry. However, the chemistry of α,β -epoxysilanes has received considerable attention. α,β -epoxysilanes⁷⁹ first described in 1958, were reported only occasionally until the mid 1970's when their reactions began to attract synthetic interest. These reactions include hydrolysis to carbonyl compounds⁸⁰, regiospecific ring opening reactions to give β -hydroxysilanes⁸¹ and their use as vinyl cation equivalents⁸². Like simple epoxides, α,β -epoxides are easily prepared by epoxidation of carbon-carbon double bonds⁸³, from carbonyl compounds⁸⁴ and by the silylation of oxiranyl anions⁸⁵ (Scheme 1.30).



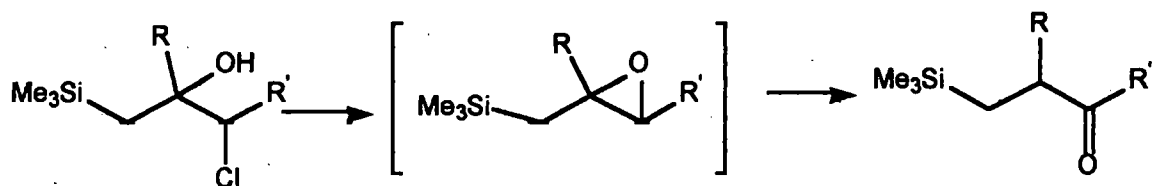
Scheme 1.30

An attempt to isolate a β,γ -epoxysilanes was unsuccessful⁸⁶. It has been reported that peroxy acid epoxidation⁸⁷ of allylsilanes produced allyl alcohols presumably via β,γ -epoxysilanes (Scheme 1.31)



Scheme 1.31

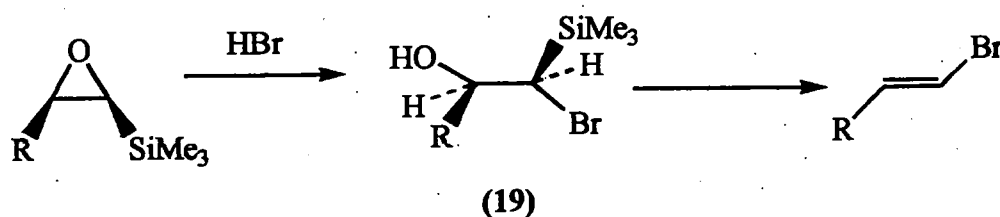
Under much milder epoxidation conditions, Hudrlik was able to isolate β -silyl carbonyl compounds⁸⁸ (scheme 1.32).



Scheme 1.32

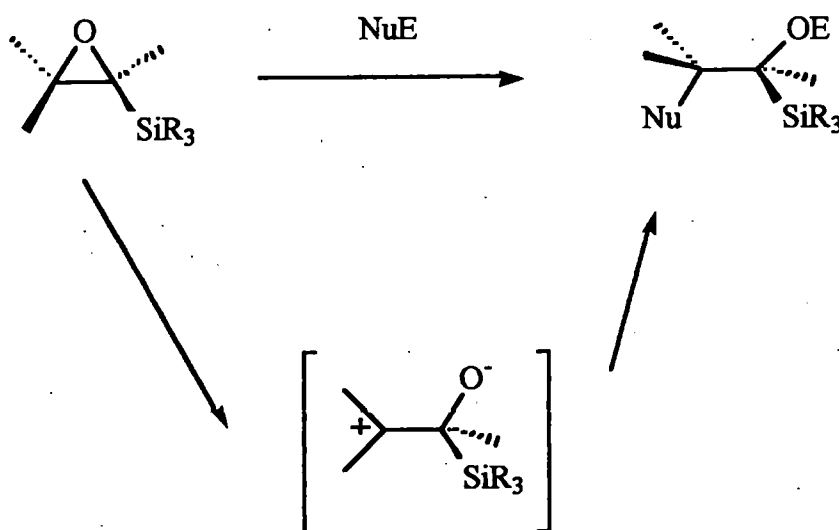
1.4.2 Ring-opening reactions of silylepoxides

Like simple epoxides, α,β - epoxysilanes undergo ring opening with a variety of reagents. With simple epoxides, the regiochemistry of ring opening under acidic conditions is influenced strongly by the relative stabilities of the two possible carbocations, while the regiochemistry under strongly nucleophilic conditions is influenced largely by steric hindrance. With α,β - epoxysilanes, where silicon is exerting a powerful directing effect, a high preference for α C - O opening has been observed^{89,90} under both acidic and nucleophilic conditions (Scheme 1.33).



Scheme 1.33

On the basis of the stability of cations β to silicon, one might expect β - cleavage to dominate via an S_N1 pathway as in Scheme 1.34.

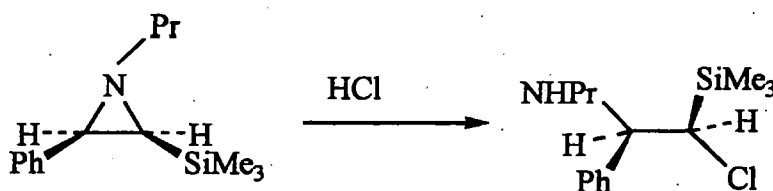


Scheme 1.34

However, the relative orientations of the C-Si bond and the developing positive charge are such that hyperconjugative overlap is minimal. A good review⁹¹ of the chemistry of α,β -epoxysilanes has been published by Hudrlik.

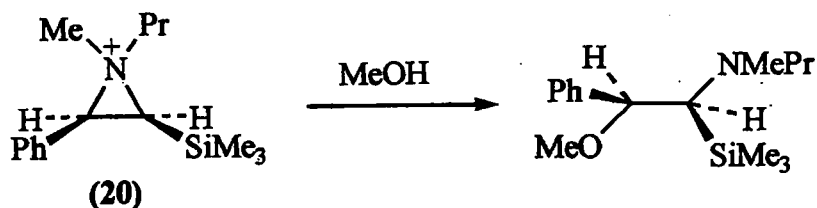
1.4.3 Synthesis and reactions of silylsubstituted aziridines

Very little work on the synthesis and reactions of silyl-substituted aziridines has been reported to date, although aziridines in general have been extensively studied. As a consequence we were interested in studying the chemistry and the synthetic potential of silyl-substituted aziridines. Novel routes for the synthesis of 2-trimethylsilylaziridines were developed earlier by my predecessors in our research group (details in chapter 3). Kyle⁹² and Soobramanien⁹³ observed that the 2-trimethylsilylaziridines also undergo α -C-N cleavage predominantly, similar to α,β -epoxysilanes. They are the only two workers to publish results on ring opening reactions of silyl aziridines to date. An example is given in Scheme 1.35.



Scheme 1.35

However, in the case of the silylaziridinium salt **20**, β -C-N cleavage occurs ahead of the O-C-bond formation in the transition state which thus has considerable sp^2 character. This S_N1 like mechanism prevails because resonance stabilization by the phenyl group becomes more important (Scheme 1.36).

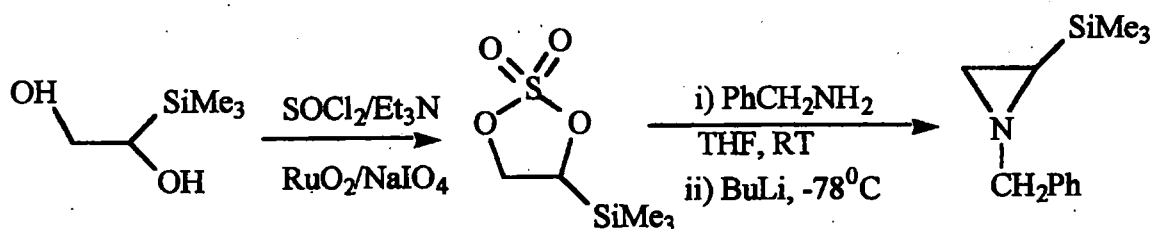


Scheme 1.36

As with β,γ -epoxysilanes, only Lukevics⁹⁴ has been able to synthesise and isolate β,γ -silylaziridines, but there is no report of their ring-opening reactions.

1.5 Synthesis of cyclic sulphates

Another interesting class of heterocyclic compounds, with similar chemistry to epoxides, are cyclic sulphates⁹⁵. Silyl derivatives of these compounds are rare and hence their chemistry has not been extensively studied. Recently, 1-trimethylsilyl ethylene-1,2-sulphate⁹⁶ was synthesised in our laboratory using a modification of the Sharpless procedure⁹⁷. This was subsequently converted to a silylaziridine, Scheme 1.37. As far as we know this is the only reported silyl substituted cyclic sulphate.



Scheme 1.37

We have been able to synthesis cyclic substituted cyclic sulphate via a different route and subsequently convert to silylaziridine (details in chapter three).

1.6 Synthesis of sily-sultones

Sultones are the analogues of lactones and, as with lactones, there exist α -, β -, γ -, and δ -sultones together with numerous cyclic sulfonates. Sultones, generally behave like open-chain sulphate esters and are excellent alkylating agents, reacting with bases and nucleophiles to produce the ring-opened sulfonate derivatives⁹⁸. There is a considerable interest in the chemistry of sultones, as they have great potential as surfactants⁹⁹, as precursors of surfactants¹⁰⁰ or anti-static agents¹⁰¹. As far as we know, no silylated sultone has been reported in the literature

1.7 Scope of the Thesis

This thesis has been divided into five chapters for convenience, with Chapter One, serving as an introduction to the whole thesis.

In Chapter Two, I examined the importance of the α silyl anion in controlling the outcome of reactions of α -vinyl carbanions with carbonyl compounds. Patricia Kyle, my predecessor had started the work but only went as far as reacting α -trimethylsilyl vinyl carbanions with various acylating agents. I repeated her work to confirm her observations and also developed the work further to react the carbanion with α,β - unsaturated carbonyl compounds before quenching with the various acylating agents. The effect of reaction conditions on the product distribution was also studied.

In Chapter Three, I report the synthesis of 2-[(trimethylsilyl)methyl]aziridines from allylsilanes. This is an extension of the work previously carried out by Marie-Claire Soobramanien and Patricia Kyle on the synthesis of 2-trimethylsilylaziridines from vinylsilanes. In this chapter, I also examine further the ability of a silicon to stabilise a positive charge in the α or β position. Systems containing both vinyl and allylic moieties were synthesised and reacted with various electrophilic reagents. The nature of the products formed gave an idea of which effect is predominant. In view of the rich

chemistry of cyclic sulphates and sultones and the lack of reported silyl derivatives, I developed a novel and facile route for the synthesis of these compounds and the subsequent conversion to corresponding aziridines, also detailed in Chapter Three. The ring opening reactions of 2- [(trimethylsilyl)methyl]aziridines with different electrophilic and nucleophilic reagents is discussed in Chapter Four. Full details of all the experiments carried out are reported in Chapter Five.

Chapter One References

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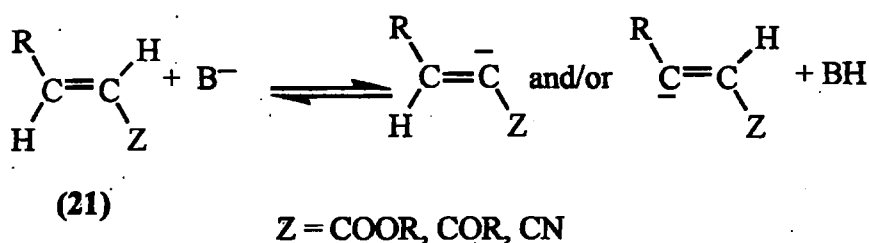
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Reactions of α -trialkylsilylvinyl carbanions with carbonyl compounds.

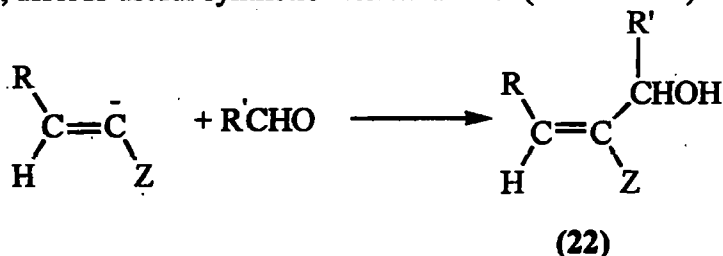
2.1 Introduction

Carbanions generated from activated vinyl systems by proton abstraction have recently been used as nucleophiles in organic synthesis^{1,2} (Scheme 2.1).



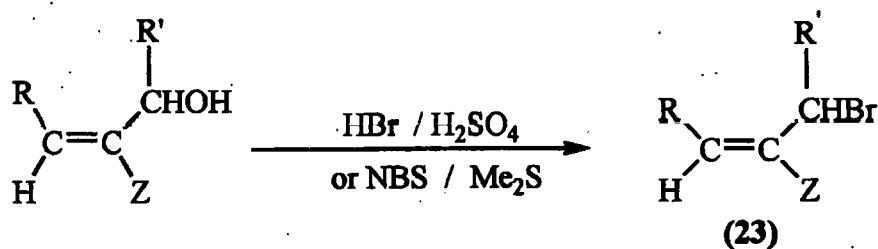
Scheme 2.1

The difficulty is preventing the isomerization of the vinyl carbanion, prior to its reaction with electrophiles, so that the geometry of the original olefin is retained in the final product³. The reaction of the vinyl carbanion with suitable electrophiles, such as carbonyl compounds, affords useful synthetic intermediates⁴ (Scheme 2.2).



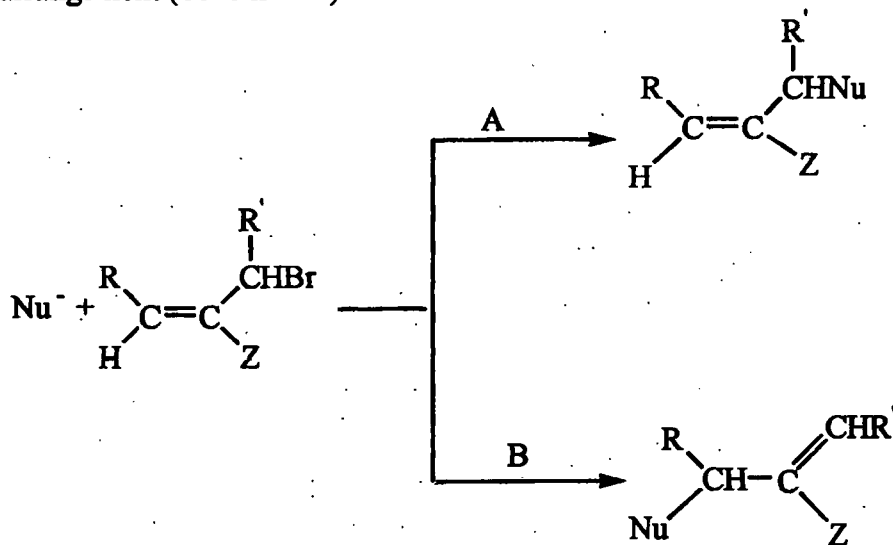
Scheme 2.2

For example, **22** can be transformed into the bromo-derivative **23**, which is a versatile synthetic intermediate (Scheme 2.3).



Scheme 2.3

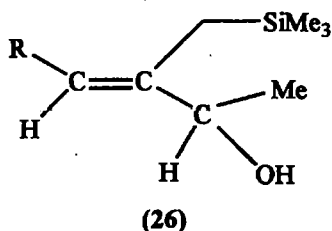
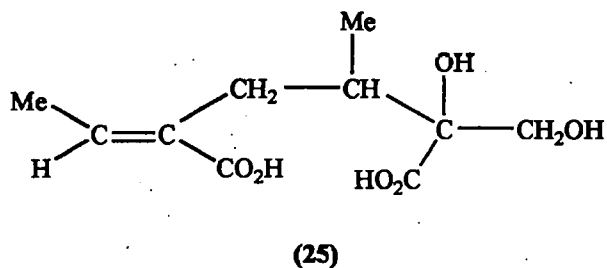
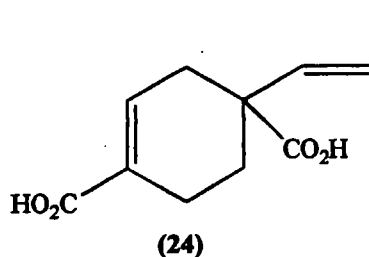
The usefulness of **23**, lies in the ability of nucleophiles to attack either the allylic carbon (normal attack; path A) or the vinyl carbon (C-3 attack; path B) with a resultant rearrangement (Scheme 2.4).



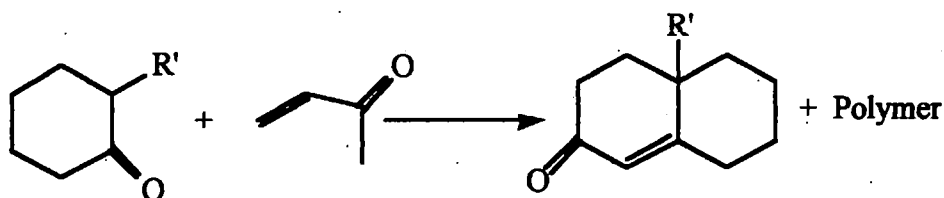
Scheme 2.4

The intermediate **23**, has been widely employed in the synthesis of natural products such as mikanecic acid **24**, retronecic acid **25** and also in the synthesis of the highly

functionalised allylsilanes **26** which are useful synthetic intermediates and have many applications. A good review for the synthetic utility of vinyl carbanions has been written by Drewes⁵.



The annulation of 2-alkylcyclohexanone with methyl vinyl ketone and its homologues is an important route to fused polycyclic systems⁶ (Scheme 2.5).

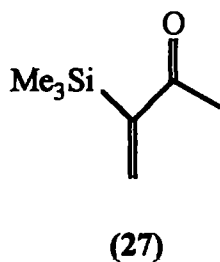


Scheme 2.5

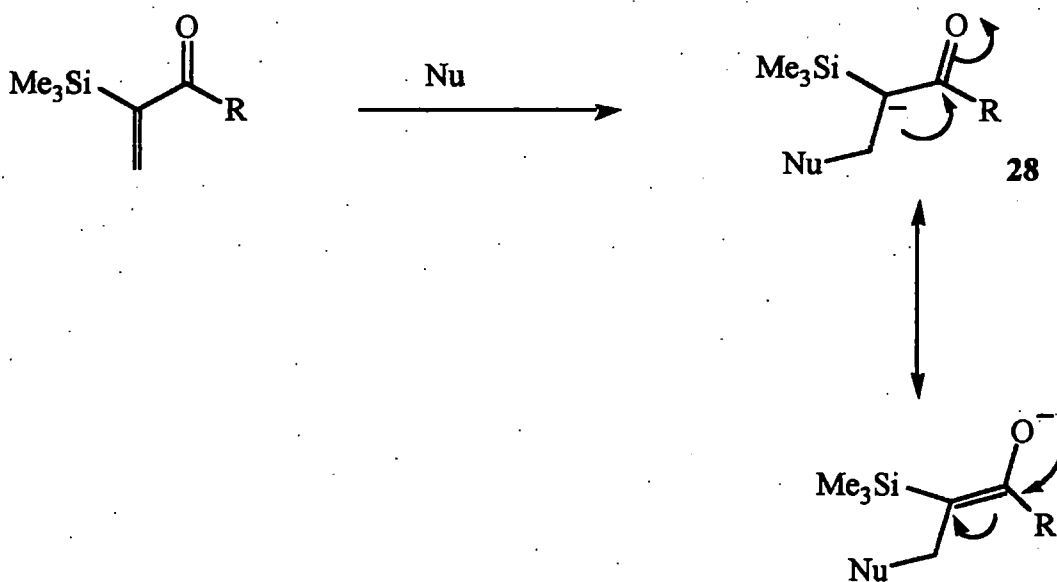
The regioselective addition of enolate ions to ordinary vinyl ketones is not normally very successful owing to the tendency of vinyl ketones to polymerise under aprotic conditions.

They also undergo rapid proton transfer and consequently, enolate regioselectivity is eliminated. In view of the important synthetic applications of α,β -unsaturated systems in annulation reactions, there is a need to stabilize the carbanion formed, hence preventing or reducing the degree of polymerization.

Stork and Ganem have used α -trialkylsilyl vinyl ketone **27** to obviate the polymerization problem⁷.

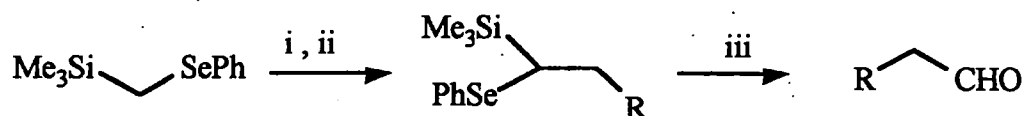


The carbanionic resonance form **28** is stabilized⁸ therefore reducing the reversibility of the reaction (Scheme 2.6).



Scheme 2.6

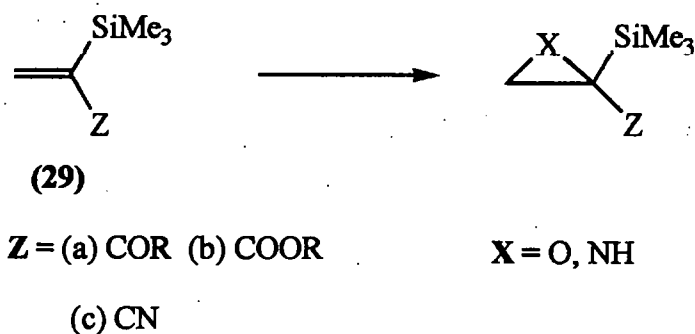
The α -ketonic silyl group in the product can be displaced very readily by nucleophiles. It has also been shown that the phenylselenosilyl carbanion reacts with primary alkyl bromides and iodides to give the corresponding aldehyde via treatment with hydrogen peroxide (Scheme 2.7).



(i) $\text{LiN}(\text{i-Pr})_2$ -THF, -78°C (ii) RCH_2X (iii) 30%w/w H_2O_2

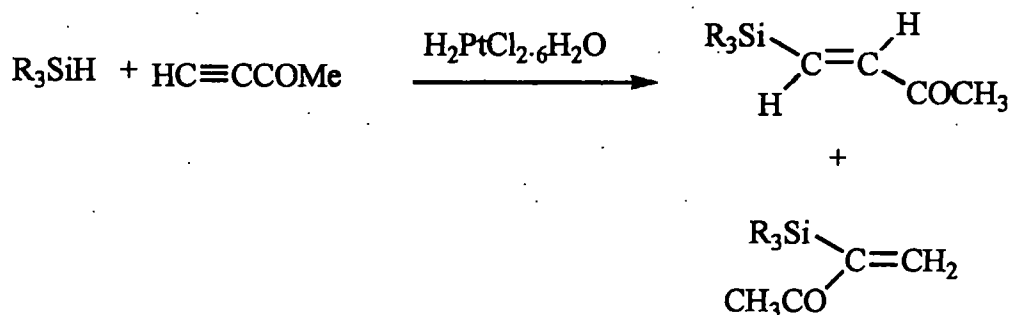
Scheme 2.7

α,β -Unsaturated carbonyl compounds having silyl groups directly attached to the carbon-carbon double bond **29** are also useful precursors to the corresponding epoxides and aziridines (Scheme 2.8).



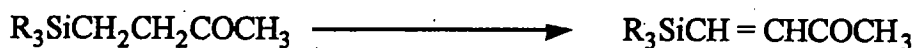
Scheme 2.8

Some years ago, several α,β -unsaturated silylated carbonyl compounds were prepared by the hydrosilylation of acetylenic carbonyl compounds. However, the reaction led to a mixture of α - and β -silylvinyl carbonyls which proved very difficult to separate⁹ (Scheme 2.9)



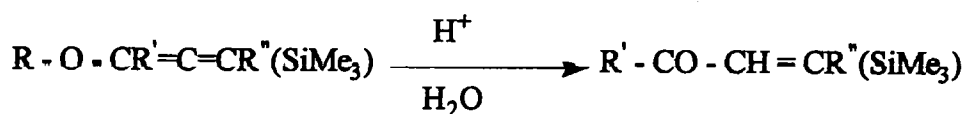
Scheme 2.9

More recently, Felix and Weber¹⁰, have described a different synthetic approach to β -silylvinyl ketones involving dehydrogenation of the saturated γ -ketosilanes (Scheme 2.10).



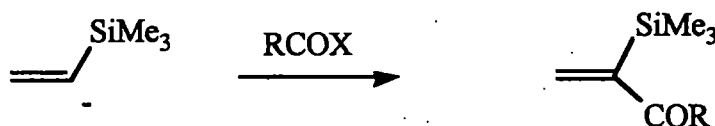
Scheme 2.10

Another route recently used to prepare β -silylvinyl ketones and aldehydes involved the hydrolysis of silylallenyl ethers¹¹ (Scheme 2.11).



Scheme 2.11

A more generally applicable route to both α - and β -trialkylsilyl carbonyl compounds would be through the coupling of trialkylsilylvinyl carbanions with carboxylic acid derivatives (Scheme 2.12). The generation of α -silyl carbanions has been extensively studied by Peterson¹² and Chan¹³.



Scheme 2.12

However, the formation of such α,β -unsaturated carbonyl systems in the presence of carbanions may lead to further addition either 1,2- or 1,4. For example, dithianes undergo exclusively 1,2-additions¹⁴, whereas anions of protected cyanohydrins give mixtures of 1,2 and 1,4 -addition products¹⁵. Although these reactions have been developed into important synthetic methodologies, the requirements for direct or conjugate addition have not been clearly identified. Schultz and his group¹⁶, have shown, however, that by simple structural modification and careful control of reaction temperature, it is possible to direct ester enolates to give either the direct or conjugate addition products.

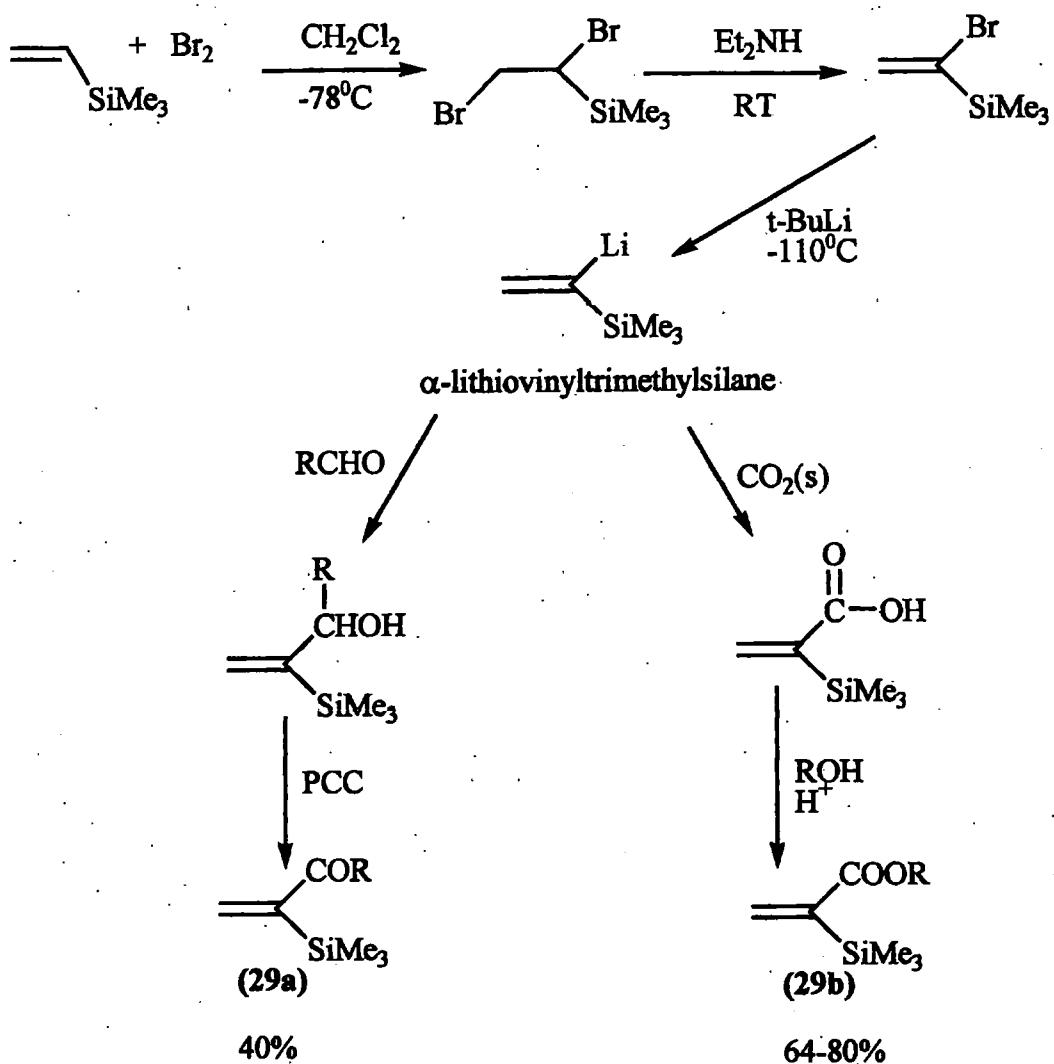
As part of our studies of small ring trialkylsilyl-substituted heterocycles, we needed to obtain compounds such as **29**. We thus undertook a study of the susceptibility of these compounds to undergo further reactions when formed from α -trialkylsilylvinyl carbanions.

2.2 Results and discussion

This section describes in detail the synthesis of trimethylsilyl α,β -unsaturated carbonyl compounds **29**, by the generation of an α -trimethylsilylvinyl carbanion and its subsequent reactions with carbonyl compounds. Also described in this section is the effect of reaction condition on product distribution.

2.2.1 Synthesis of trimethylsilylvinylmethylketone and ethyl-2-(trimethylsilyl)acrylate.

The intermediate α -bromovinyltrimethylsilane, was prepared by the selective dehydrobromination of 1,2-dibromotrimethylsilyl ethane, which was prepared by the bromination of vinylsilane in dichloromethane at -78°C . This versatile intermediate was subsequently converted to α -lithiovinyltrimethylsilane by the reaction of *tert*-butyllithium with the α -bromovinyltrimethylsilane in dry THF at -110°C . Reaction of this carbanion with acetaldehyde at -110°C followed by hydrolysis gave the vinyl alcohol which was oxidised with pyridinium chlorochromate in dichloromethane to give the trimethylsilylvinylmethyl ketone **29a**. Reaction of α -lithiovinyltrimethyl silane with solid carbon dioxide, gave the 2-(trimethylsilyl)acrylic acid. Reaction of this with acidified alcohol gave the 2-(trimethylsilyl)acrylate **29b** in 80% yield (Scheme 2.13).



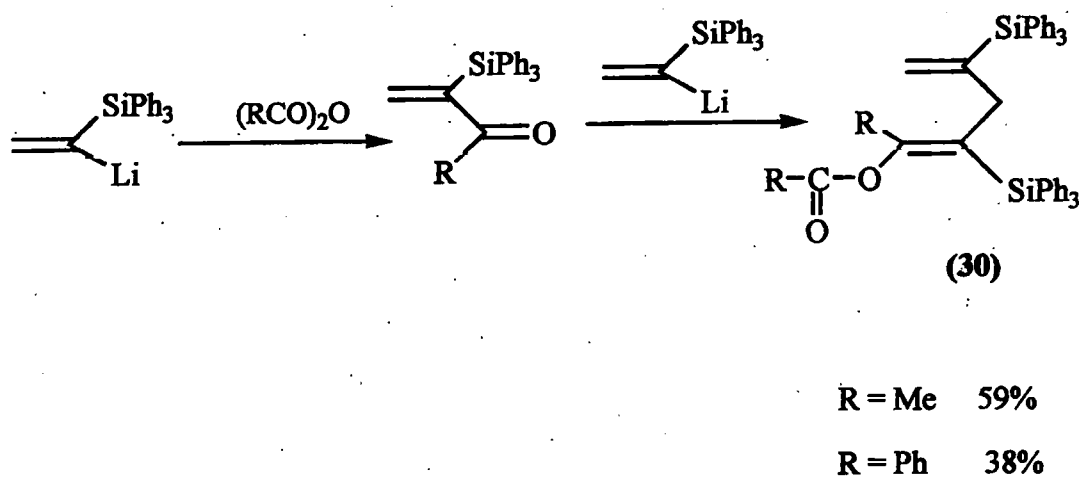
Scheme 2.13

2.2.2 Reactions of the α -trimethylsilylvinyl carbanion with carboxylic acid derivatives.

The α -trimethylsilylvinyl carbanion, was reacted with various carboxylic acid derivatives, in order to check the susceptibility of these products to undergo further conjugate addition if formed in the presence of excess carbanions.

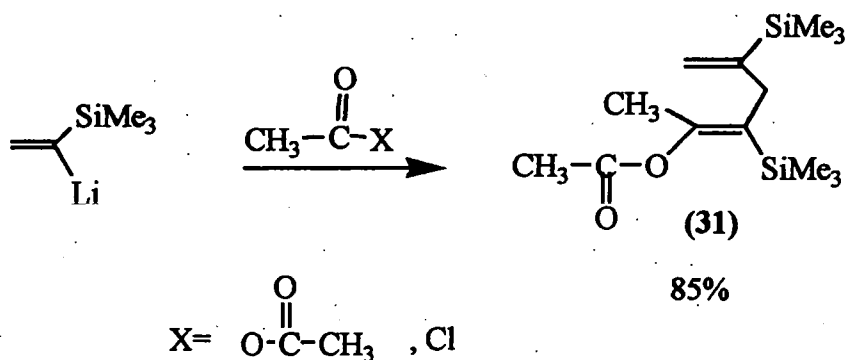
2.2.2.1 Reaction of the α -trimethylsilylvinyl carbanion with anhydrides and acid-chlorides.

Brook and Duff have shown that whilst reaction of α -triphenylsilylvinyl carbanions with anhydrides does indeed give the corresponding ketones, the presence of excess of the carbanion leads to further conjugate addition¹⁷ (Scheme 2.14).



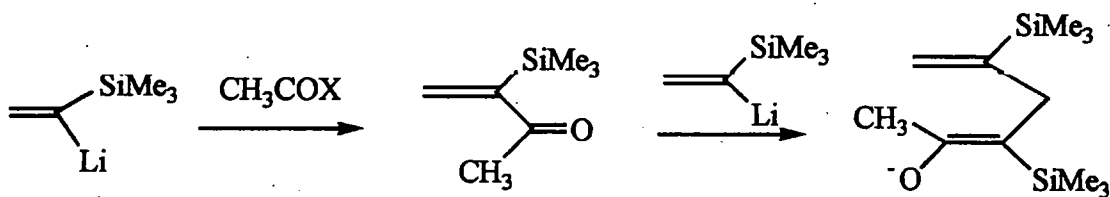
Scheme 2.14

They found that when α -triphenylsilylvinyl carbanion was reacted with ethanoic or benzoic acid anhydrides at room temperature, only the product of conjugate addition followed by oxygen acylation was obtained. However, at -78°C , the vinyl-ketone could be obtained in 82% yield. We repeated this work using α -trimethylsilylvinyl carbanions obtained from the corresponding vinylbromide using *tert*-butyllithium in THF at -110°C . We isolated the product of conjugate addition and subsequent acylation in almost quantitative yield. Reaction with ethanoyl chloride gave a similar product (Scheme 2.15)



Scheme 2.15

In these experiments, the α -trialkylsilylvinyl carbanion is formed in-situ and the carboxylic acid derivative added dropwise. Thus, if the carbanion reacts with the carboxylic acid derivative as soon as it is added to give the α,β -unsaturated ketone, there will be an excess of the carbanion remaining that will react further via conjugate addition, before more of the carboxylic acid derivative is supplied (Scheme 2.16).

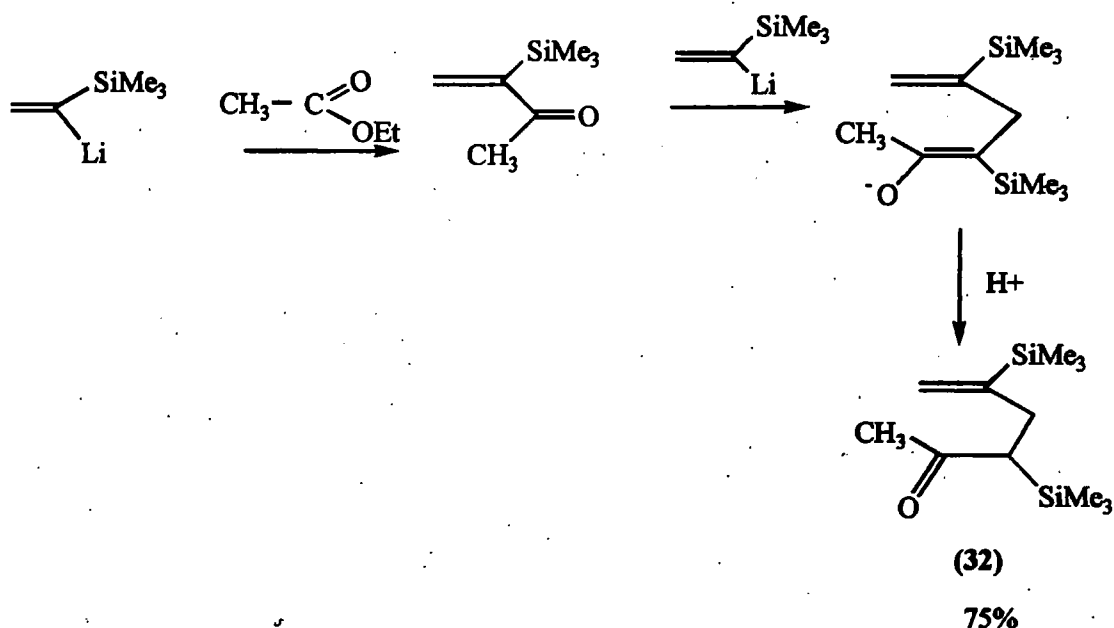


Scheme 2.16

No product of 1,2 addition to the α,β -unsaturated ketone was obtained. The trimethylsilyl group ensures that the conjugate addition is thermodynamically favourable. Further acylation of the enolate leads to attack at the oxygen rather than the corresponding Claisen reaction. This behaviour has been observed previously with reactive acylating agents¹⁸.

2.2.2.2 Reaction of the α -trialkylsilylvinyl carbanion with esters and carbamate derivatives.

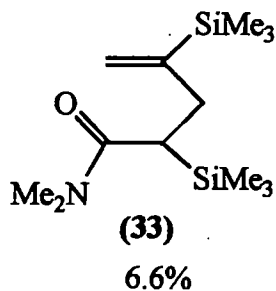
We examined a number of less reactive acylating agents to discover if the same behaviour was observed. Reaction of the α -trialkylsilylvinyl carbanion with ethyl ethanoate gives the corresponding product of conjugate addition, that is, there is no further acylation (Scheme 2.17).



Scheme 2.17

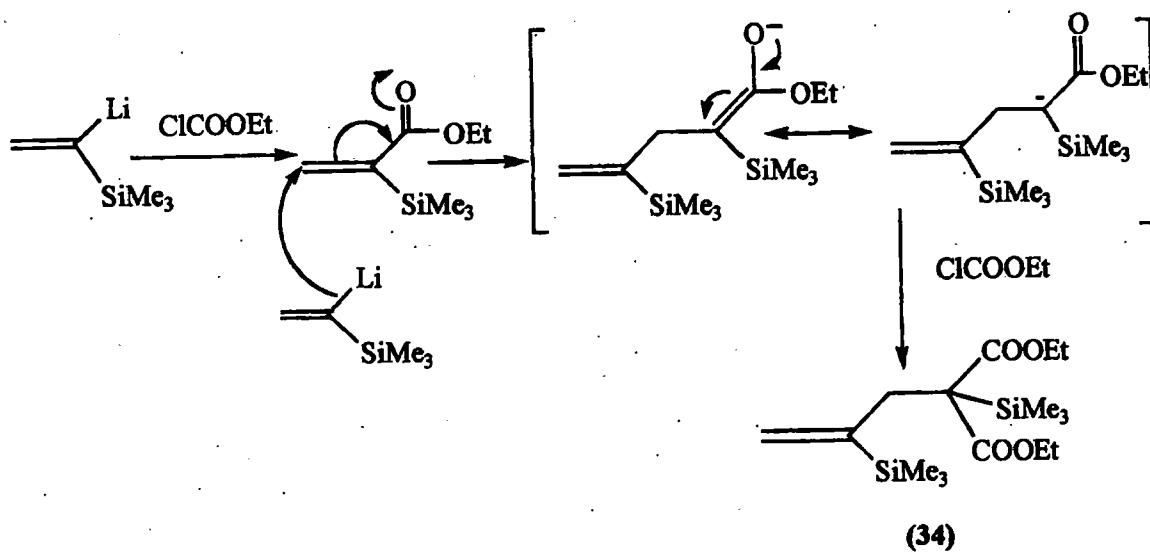
In this case, the less reactive ester may have been expected to undergo a Claisen reaction to

give the diketone. However, under the conditions of the experiment, no such product was observed, which may reflect the reduced reactivity of the enolate owing to stabilisation by the adjacent trimethylsilyl group. A similar outcome was observed using dimethyl - carbamoyl chloride which gave the amide **33**, although in poor yield.



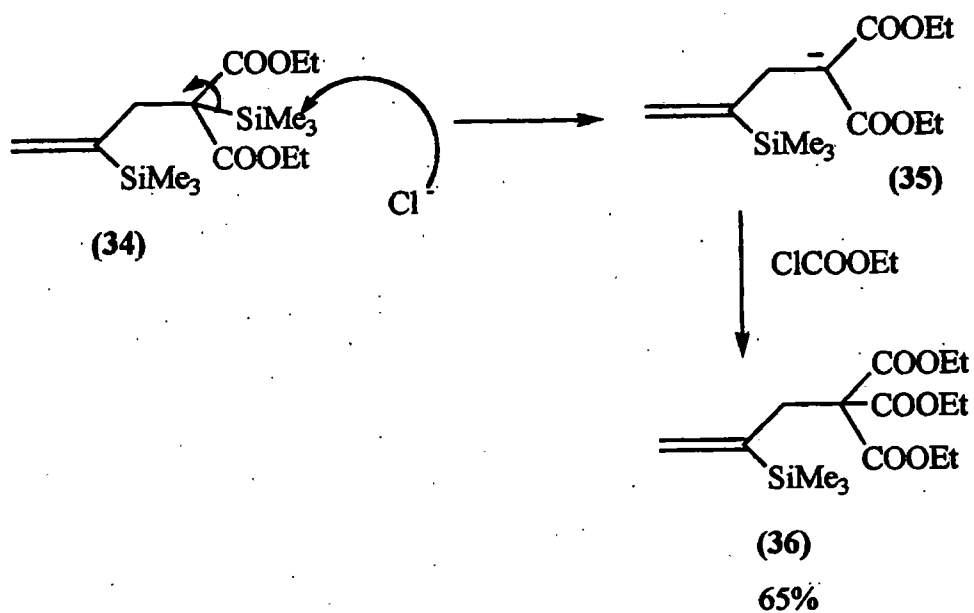
2.2.2.3 Reaction of the α -trialkylsilylvinyl carbanion with alkyl chloroformates.

The use of more reactive acylating agents than esters again led to further reaction of the conjugate addition product. In this case, instead of attack at the oxygen, carbon acylation was observed to give the diester, **34**. This preference for carbon rather than oxygen acylation is common with alkyl chloroformates¹⁹. Further reaction is observed in this case not only because the acylating agent is more reactive, but also because the ester enolate is more reactive (Scheme 2.18).



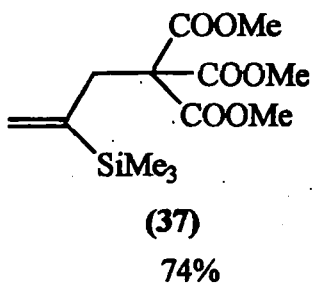
Scheme 2.18

Interestingly, this diester reacts further via a chlorodesilylation to give a malonate type enolate 35, which is then converted to the triester 36 (Scheme 2.19).



Scheme 2.19

Such formation of tricarboxylic acids has been reported,²⁰ however this is the first instance where the carbanion is generated through chlorodesilylation. The same type of product 37 is obtained if methyl chloroformate is substituted for ethyl chloroformate.

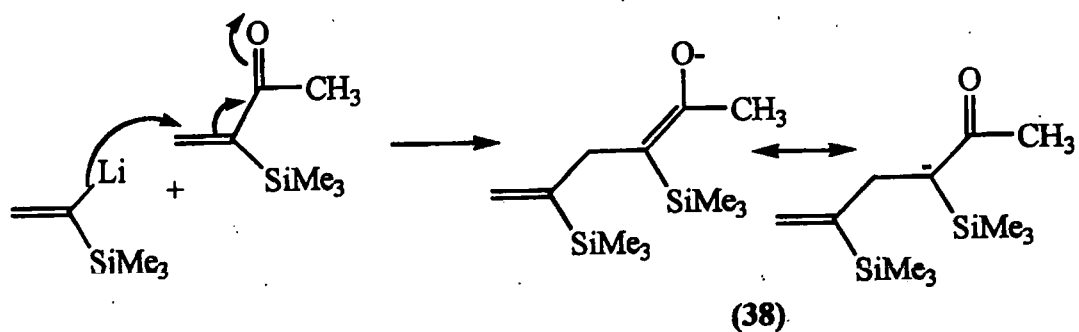


2.2.3 Reaction of the α -trialkylsilylvinyl carbanion with α,β -unsaturated carbonyl compounds.

In order to confirm that our earlier mechanistic arguments were correct, we reacted the α,β -unsaturated carbonyl compounds 29, prepared as shown in Scheme 2.13, with the α -lithiotrimethylsilylvinyl carbanion and subsequently quenched the resulting enolate with various carbonyl compounds.

2.2.3.1 Reaction of the α -trimethylsilylvinyl carbanion with an α,β -unsaturated ketone

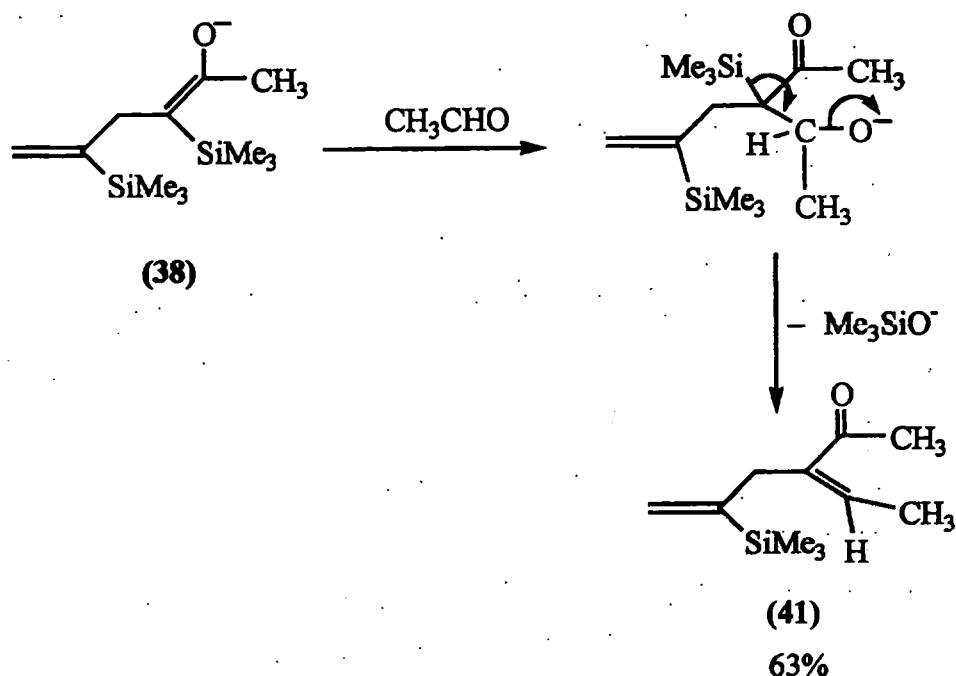
Addition of one equivalent of α,β -unsaturated ketone, to the α -lithiovinyltrimethylsilyl carbanion at -110°C , led to a conjugate addition product 38 (Scheme 2.20).



Scheme 2.20

The enolate is stabilised both electronically and sterically by the trimethylsilyl group, thus making it less reactive than the starting carbanion²¹. The enolate, could be quenched with water to give the bis-trimethylsilyl ketone 32, or treated with an ethyl chloroformate or methylchloroformate to give the ketoesters 39 and 40 respectively. Quenching the adduct with acetic anhydride gave the oxygen acylated product 31 (Scheme 2.21).

Interestingly, under the conditions for formation of 39 and 40, no desilylation to give the more stable enolate ion was observed, as might be expected. This may be due to the lower concentration of chloride ion present. Reacting enolate 38 with acetal-dehyde gave the dienone 41. This is formed as a result of the intermediate alcohol undergoing a Peterson reaction, as shown in Scheme 2.22.

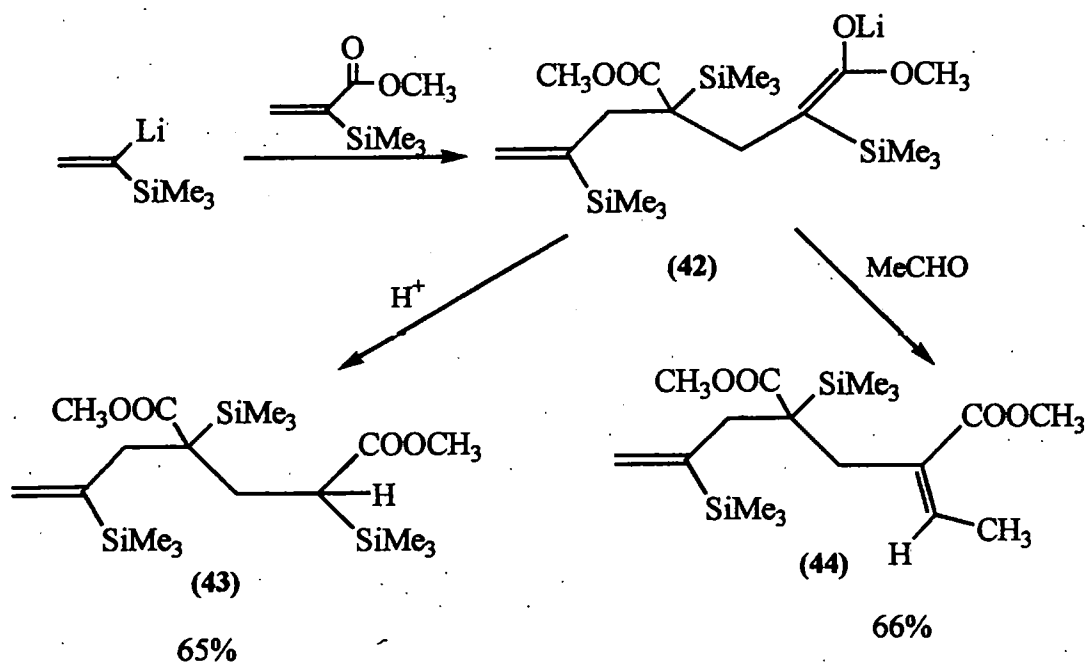


Scheme 2.22

Similar products of a sequential Michael addition and Peterson condensation of a silyl vinyl ketone have been reported by Tsuge²².

2.2.3.2 Reaction of the α -trialkylsilylvinyl carbanion with an α,β -unsaturated ester.

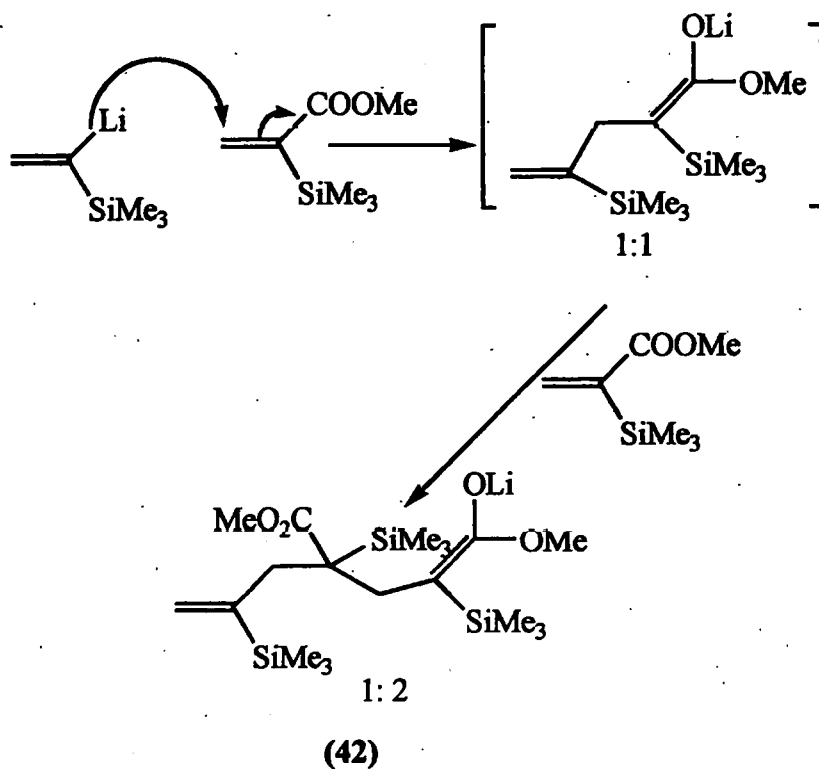
Methyl 2-(trimethylsilyl)acrylate, can serve as a highly reactive and base-stable acceptor in Michael additions with organometallics. Even with equivalent amounts of the α,β -unsaturated ester and the carbanion, we found that the 1:2 adduct **42** is produced. This type of behaviour has been observed before in the reaction of methyl 2-(trimethylsilyl)propenoates with organomagnesiums and lithiums²³ **43** and **44** were formed as single diastereoisomers after quenching the anion at -100°C with water and acetaldehyde respectively (Scheme 2.23).



Scheme 2.23

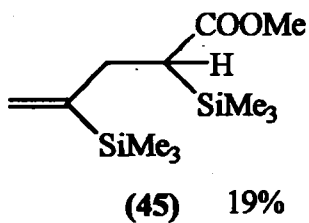
The diester **43**, corresponds to the Michael addition²⁴ of the 1:1 adduct anion with the

methyl 2-(trimethylsilyl) acrylate, followed by the subsequent diastereoselective protonation of the resulting 1:2 adduct anion (Scheme 2.24).



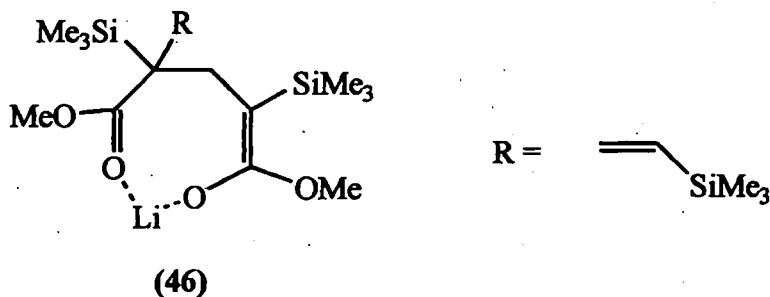
Scheme 2.24

If we stirred the enolate mixture at room temperature for one hour before quenching with water we obtained the monoester 45.



A possible mechanistic argument for the formation of the 1:2 adduct as the preferred

enolate might be that as soon as methyl 2-(trimethylsilyl) acrylate is added dropwise to the α -lithiovinyltrimethylsilane, reaction takes place to form the 1:1 adduct. This depletes the concentration of α -lithiovinyltrimethylsilane in the vicinity of the added carbonyl compounds hence the product of conjugate addition can compete successfully for the remaining carbonyl to form the 1:2 adduct **42**. This product does not undergo further reaction. The fact that monoester was isolated when the enolate mixture was warmed to room temperature before quenching, indicates that the 1:2 adduct is more likely a kinetic product and that enolate formation is to some extent reversible. The lack of further alkylation or acylation of the 1:2 adduct may arise from complexation to give the cyclic chelate **46**. Previous studies of the Michael reaction have highlighted the importance of cyclic intermediates²⁵. In this case the metal ion can be chelated in an eight-membered ring using the oxygen of the enone and the enolate.



The formation of **43** and **44** as single diastereoisomers points to the formation of a chelated species **46**, at least in the transition state, where one configuration is favoured.

2.2.4. The effect of reaction conditions on the product distribution.

We investigated the type of reaction conditions that will give exclusively the α,β -unsaturated carbonyl compound. The problems associated with the further conjugate addition of these α,β -unsaturated carbonyl compounds arise from them being formed in the presence of excess carbanion. This can be alleviated by carrying out an inverse addition. In this case, for most of the addition, the carbonyl compound is in excess and thus can compete successfully with the α,β -unsaturated carbonyl compound. This can be experimentally difficult because the carbanion needs to be kept at low temperature otherwise it will decompose. Such a situation obtains when the α -trimethylsilylvinyl carbanion is added to solid carbon dioxide to give the corresponding α,β -unsaturated acid²⁶. Such inverse additions were examined by syringing the cold carbanion into a pre-cooled solution of acetic anhydride and ethyl chloroformate, to give only the direct addition products 29a and 29b respectively. However, whilst the desired product can be formed, the yield of the α,β -unsaturated carbonyl compound is low. Changing the solvent from THF to hexane, but nevertheless employing the inverse addition procedure, led to the formation of α,β -unsaturated ester in good yield

2.2.5 Conclusion

In conclusion, we have shown that the reaction of α -trimethylsilylvinyl carbanions with carboxylic acid derivatives leads first to the corresponding α,β -unsaturated carbonyl compound. However, under the conditions of the reaction, these products undergo conjugate addition with the remaining carbanion. In our reactions we isolated mainly products of 1,4 additions. Further reaction with the acylating agent depends upon the reactivity of the enolate as well as that of the carboxylic acid derivative. Finally, control of

the conditions does allow the α,β unsaturated carbonyl compound to be isolated.

2.3 Chapter Two References

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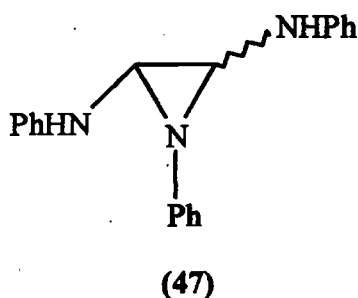
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CHAPTER THREE

Synthesis of β -trialkylsilyl-substituted aziridines.

3.1. Introduction.

Aziridines (or ethylenimines) are saturated three-membered heterocycles containing one nitrogen atom. Aziridine chemistry started in about 1875, with the exploratory work of Sebanayev, who assigned the aziridine structure 47 to the product obtained from reaction of 1,1,2,2-tetrabromoethane with aniline¹.



This provided the foundation upon which subsequent scientists could build. Notably, Lehrfeld², Ladenburg³, Abel⁴, Von Hofmann⁵, Schmidt⁶, Gabriel⁷ and Marckward⁸.

During this time a number of interesting reactions and reagents came to light. A very good review article covering this time has been published by Dermer⁹.

3.2. Physical properties of aziridines.

To fully understand the behaviour of aziridines, knowledge of their structure is very important. Two fundamental physical properties, their ring-strain and the basicity of the ring nitrogen govern the chemistry of these compounds.

The lower molecular weight, volatile, aziridines are colourless liquids with a characteristic ammoniacal odour. The dimensions of the three-member ring as determined by microwave spectra¹⁰, electron diffraction¹¹(of ethylenimine vapour) and X-ray diffraction¹² of crystalline derivatives, shows that the bond lengths (summarized in Table 3.1) are very nearly equal, hence the internal bond angles must be close to 60° compared with 111.3° for the C-N-C bond angle in diethylamine.

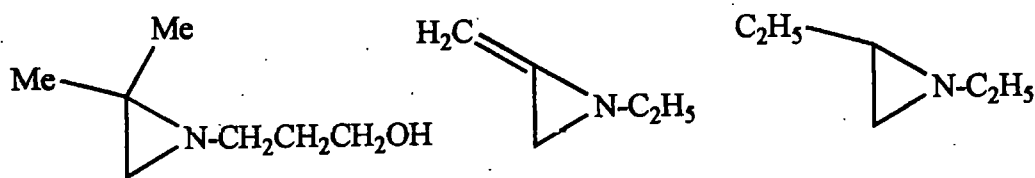
Table 3.1 **Bond lengths in Ånströms**

Bond	microwave diffraction	electron diffraction	X-ray diffraction	open-chain amines
C-C	1.480	1.48	1.463	1.54
C-N	1.488	1.49	1.510, 1.468	1.47

The C-C bond lengths shown above are generally lower than their open-chain counterparts. The resulting ring-strain is also reflected in an increase in the C-H vibration frequencies and a decrease in the N-H vibrational frequencies as determined by measurement of infrared and Raman spectra¹³. Compared to their open-chain analogues, aziridines have higher boiling points. This is attributed to enhanced hydrogen-bonding. The effect of intermolecular H-bonding in raising the boiling point is shown by comparing the values for 2-methylaziridine and 1-methylaziridine which have been found to be 66°C/760mmHg and 23.5°C/739mmHg respectively¹⁴. Ethylene oxide boils at 13.5°C. From heat of combustion data¹⁵, the strain energy has been estimated to be about 14 kcal/mol for ethylenimine. This can be compared with cyclopropane, ethylene oxide and ethylene sulfide which are 25, 13 and 9 kcal/mol respectively.

Compared to their open-chain analogues, aziridines are relatively weak bases. This fact has been described and discussed in terms of the aromaticity or electron delocalization of the 3-membered ring^{16,17}. The pK_s of alkyl aziridines are in the range 7.93-9.47, whereas

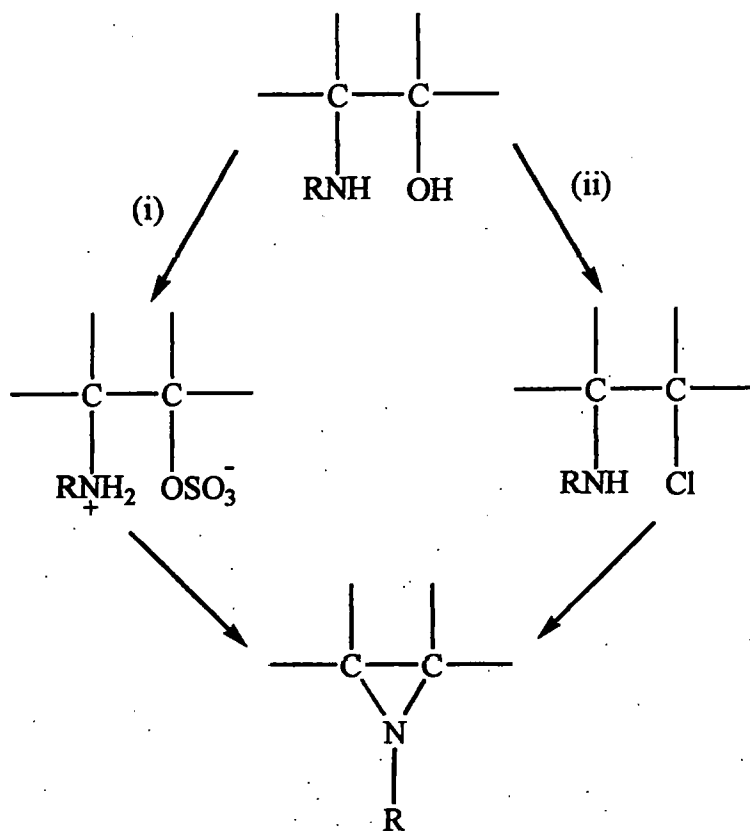
ammonia is 9.5 and dimethylamine 10.7¹⁸. The nmr spectra of N-substituted aziridines such as:



show that the substituents on the nitrogen do not lie in the plane of the ring. However, the inversion frequency is so high that resolution of such molecules, even in the most favourable of cases is likely to be possible only at temperatures below -50°C¹⁹.

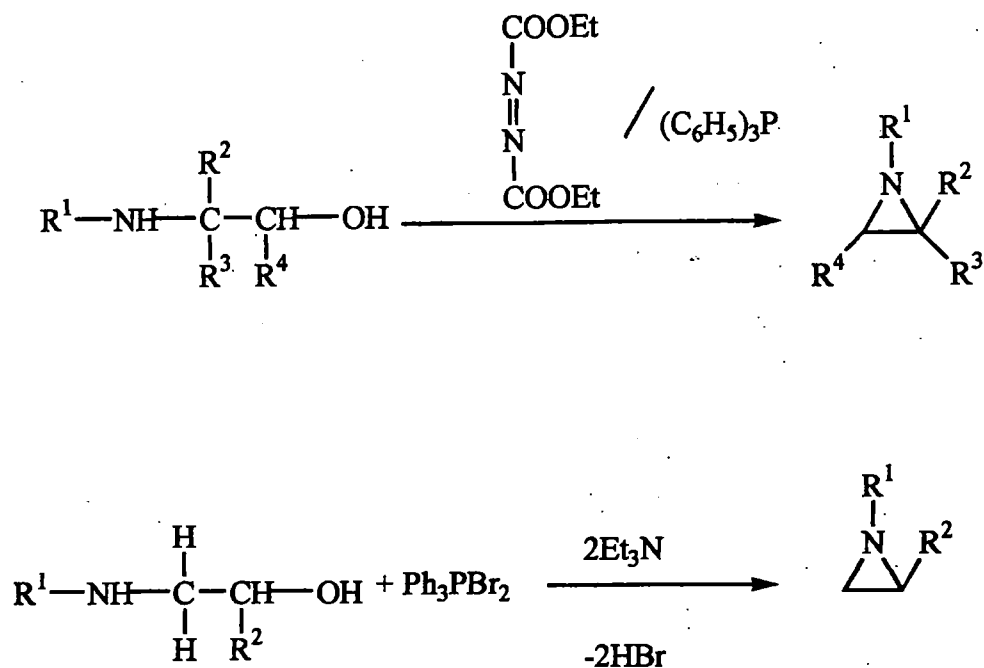
3.3 Synthesis of aziridines

A variety of methods have appeared for the synthesis of aziridines. Two of the earliest and most frequently used methods are the Wenker²⁰ and the Gabriel²¹ syntheses (Scheme 3.1). The Wenker method (route i) involves the successive reaction of β -hydroxylamines with sulphuric acid to form an intermediate O-sulphuric ester and cyclization of this using base gives the corresponding aziridine.



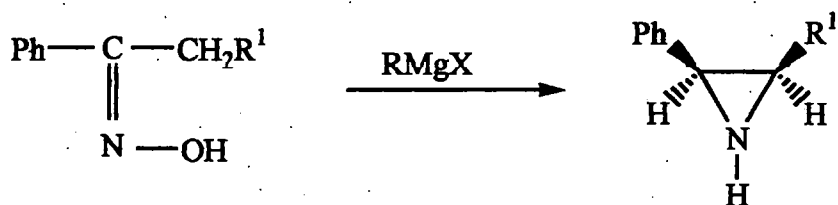
Scheme 3.1

The Gabriel method (route ii) on the other hand involves the conversion of β -hydroxylamines to a β -haloamine. Subsequent treatment of this with base gives the corresponding aziridine. Recently superior routes from amino alcohol has appeared (Scheme 3.2)²²



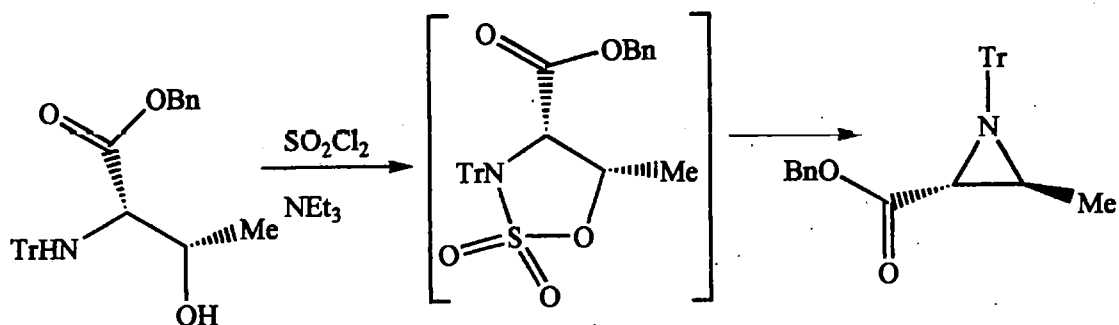
Scheme 3.2

The Hoch-Campbell²³ synthesis of aziridines is both stereo- and regio-specific. It involves the reaction of a ketoxime with a Grignard reagent (Scheme 3.3).



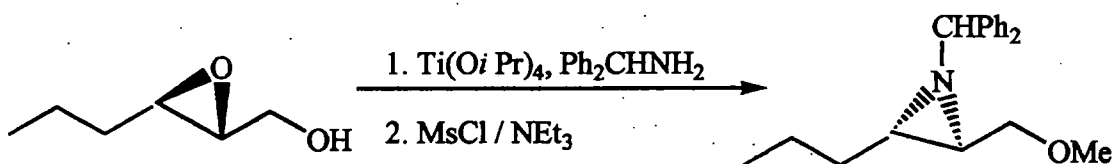
Scheme 3.3

The “one-pot” method developed by Kuyl-Yeheskiely’s group²⁴ for the synthesis of aziridines from amino acids is noteworthy for its simplicity and efficiency (Scheme 3.4)



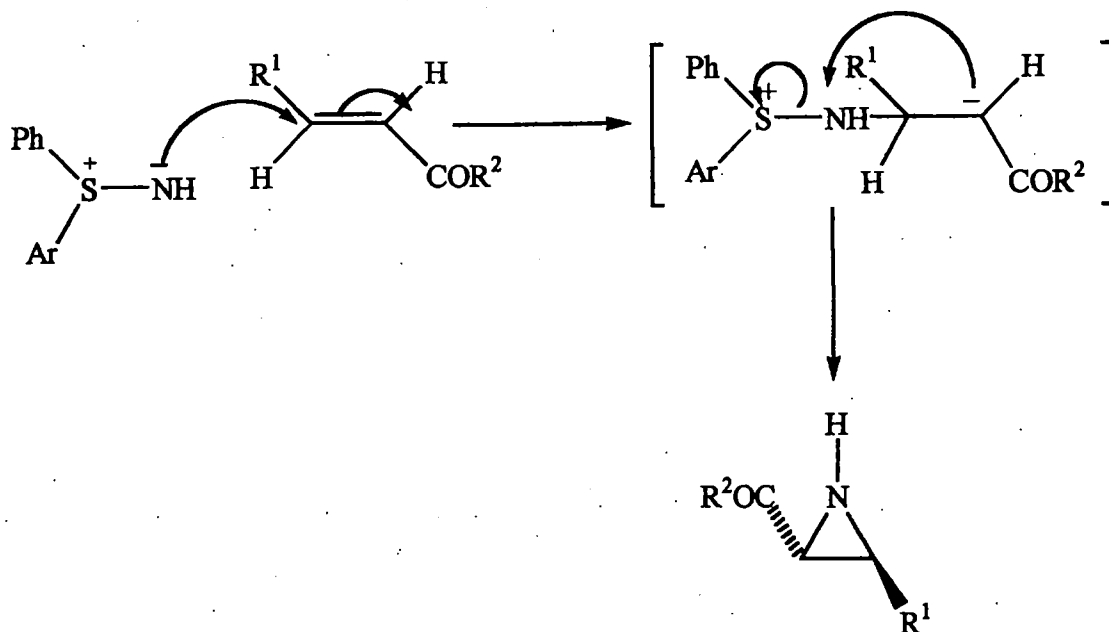
Scheme 3.4

The versatile chemistry of epoxides²⁵ has also been employed in the synthesis of aziridines (Scheme 3.5).



Scheme 3.5

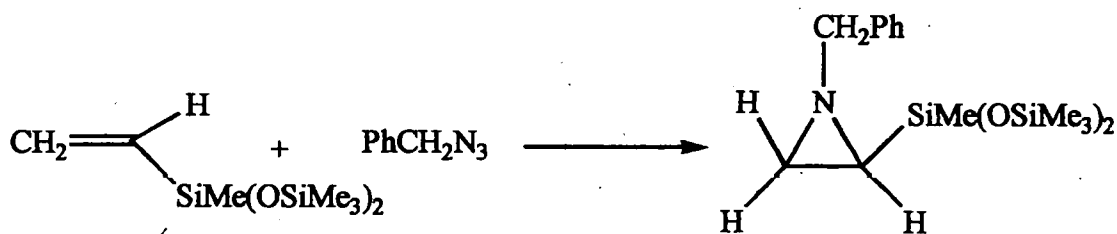
Aziridines have been prepared stereospecifically by the nucleophilic addition of a nitrogen-sulphur ylid to an alkene²⁶ via a Michael-type addition (Scheme 3.6). If a chiral sulfilimine is used, the chirality is transferred to the aziridine.



Scheme 3.6

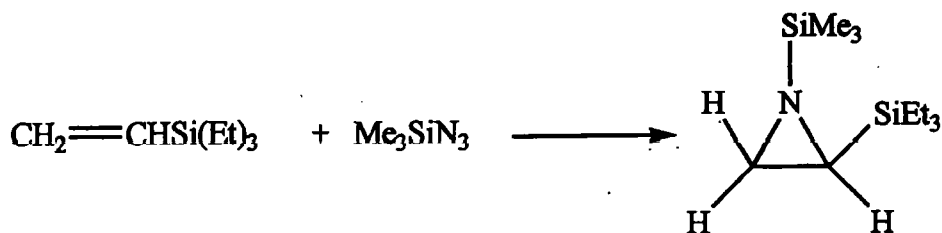
3.4. The chemistry of silylaziridines

Despite the considerable attention that aziridines has received, very little work has been reported on the chemistry of silyl-substituted aziridines. Aziridines containing a silyl group bonded to one of the ring carbons, was first reported by Andrianov and co-workers in 1964²⁷. These compounds were formed in moderate yield from the reaction of benzyl azide with (1-methyl-1-hexamethyl-disiloxy)silylethene (Scheme 4.7)



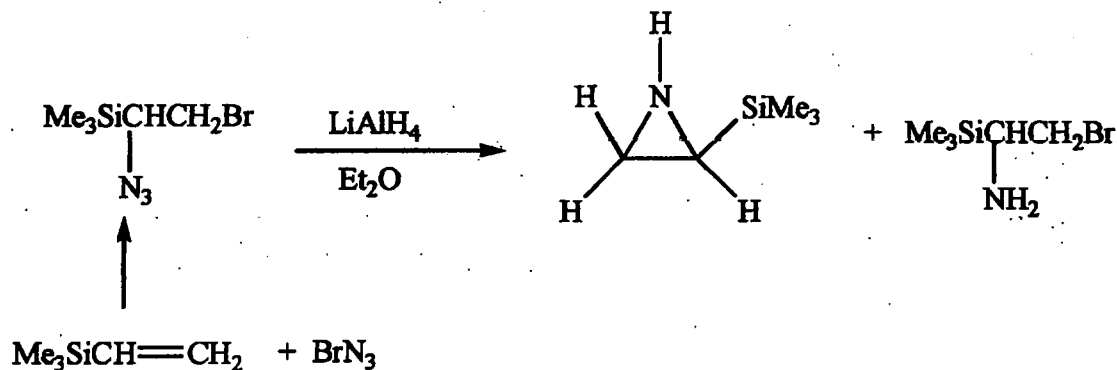
Scheme 3.7

Ettenhuber and Ruhlmann devised an alternative preparation²⁸. This involved the reaction of a vinyl silane with trimethylsilyl azide (Scheme 3.8)



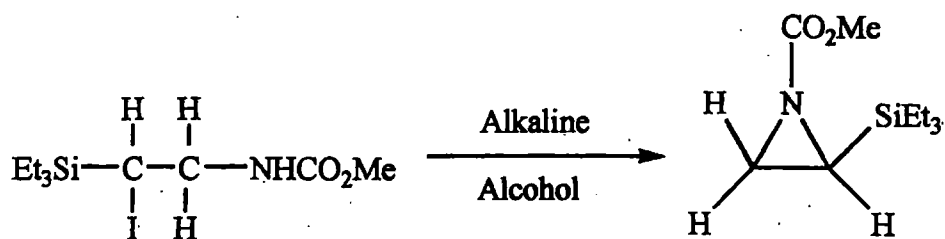
Scheme 3.8

Bassindale and co-workers have subsequently reproduced the results of Andrianov. However, they were unable to repeat the work of Ettenhuber and Ruhlmann obtaining aminosilanes instead of the proposed aziridines²⁹. Duboudin and Laporte have since prepared silylated aziridines by the reduction of α trialkylsilylbromoazides using lithium aluminium hydride³⁰ (Scheme 3.9).



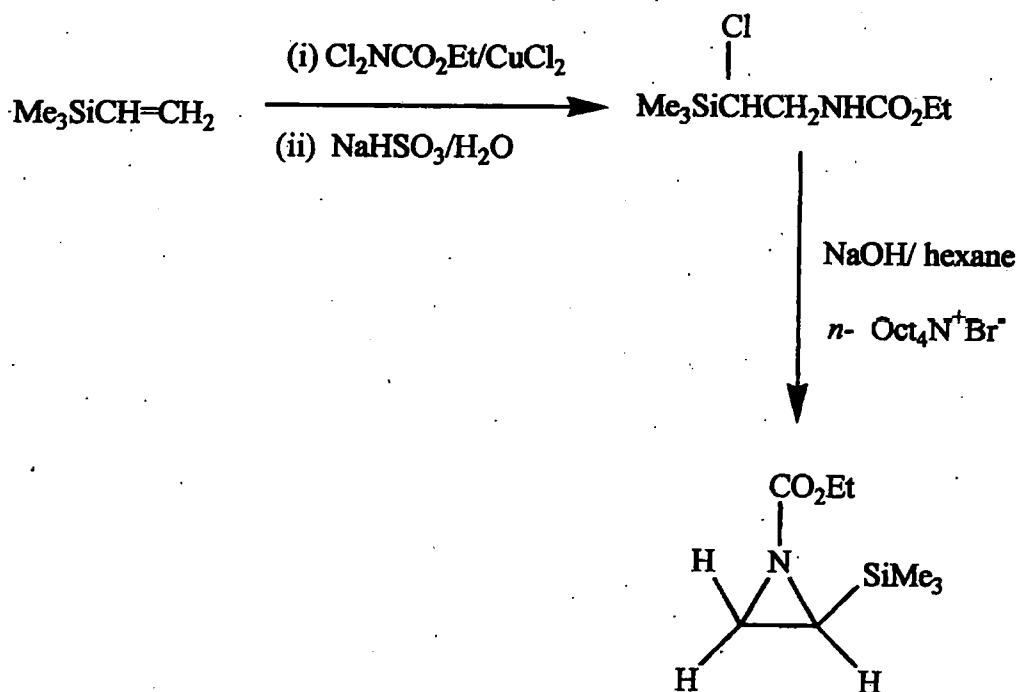
Scheme 3.9

Vakrusher and co-workers have obtained trialkylsilyl-1H-aziridines in 30% yield by the treatment of methyl-N-(2-iodo-2-triethylsilyl)ethylcarbamate with alkaline alcohol (Scheme 3.10)³¹.



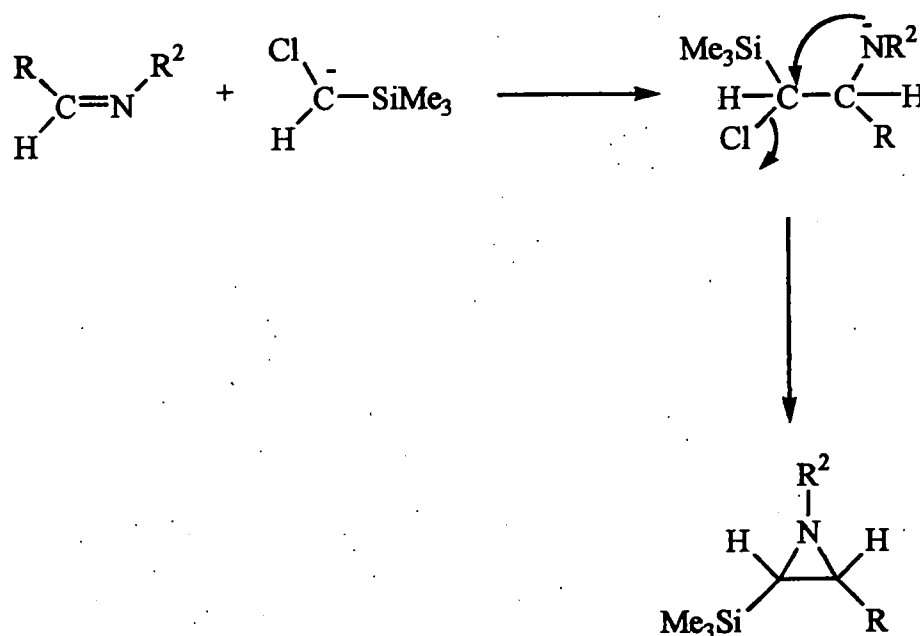
Scheme 3.10

Lukevics³² reported a phase-transfer catalysed intramolecular alkylation of Methyl (2-chloro-2-trimethylsilyl)ethylcarbamates in the presence of tetraoctylammonium bromide at room temperature to give 1-ethoxycarbonyl-2-trimethylsilylaziridine in good yield (Scheme 3.11)



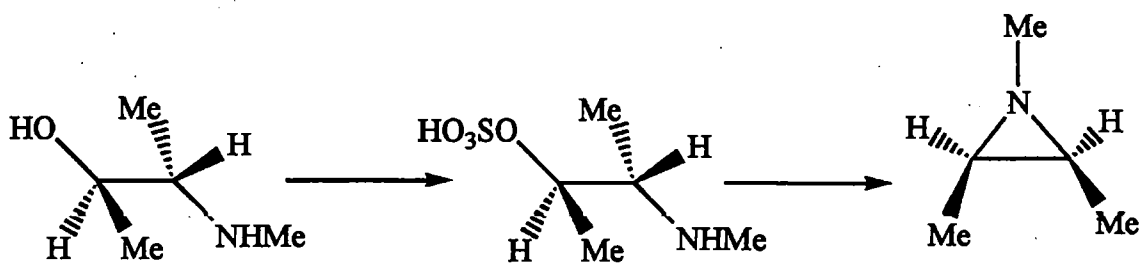
Scheme 3.11

Soobramanien³³ has synthesized a series of substituted 2-trialkylsilylaziridines by a modification of the Peterson reaction. She found that attack of α -chloromethyl-trialkylsilyl carbanion on an azomethine carbon occurs to give an intermediate, which then cyclizes to the corresponding aziridine (Scheme 3.12)



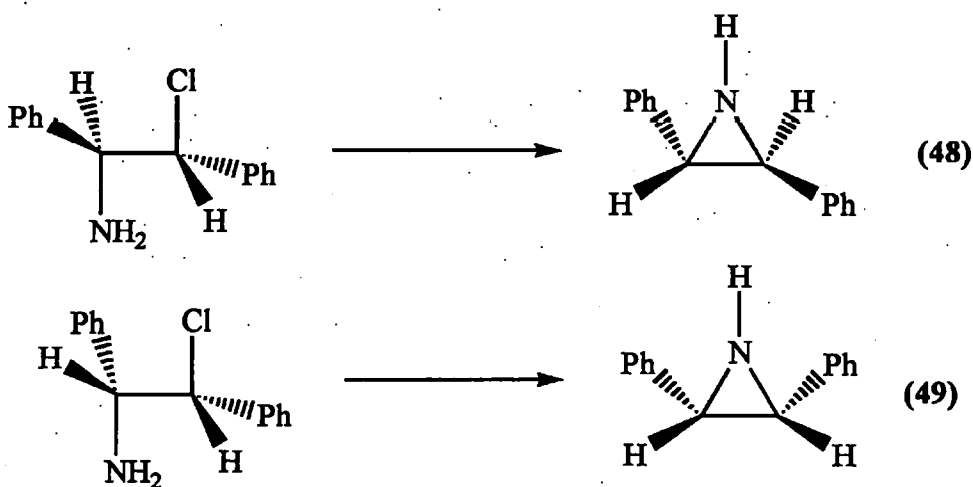
Scheme 3.12

The stereochemistry and mechanism of ring closure of 1,2-amino halides or sulphates has been studied³⁴. Lucas and collaborators^{34b} have shown that the formation of the sulphuric acid ester occurred with retention of configuration. However, ring closure involved an inversion of configuration at the β -carbon atom. They showed that optically active *erythro*-3-methylaminobutan-2-ol gave the ester, which cyclized to give only optically active *N*-methyl *trans*-2,3-dimethylaziridine (Scheme 3.13).



Scheme 3.13

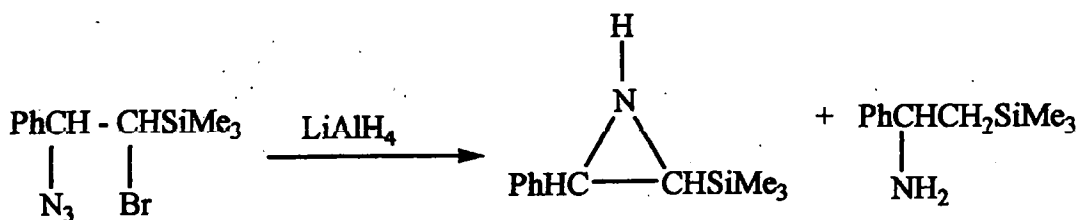
β -chloroamines (obtained from the Gabriel synthesis) have also been shown by Weissberger and Bach³⁵ to undergo ring closure to aziridines with inversion at the carbon bearing the halogen atom. They observed that cyclization of (-)-*erythro*-1-amino-2-chloro-1,2-diphenylethane led to the optically active *trans*-2,3-diphenylaziridine **48** and (-)-*threo*-1-amino-2-chloro-1,2-diphenylethane gave the optically inactive *cis*-2,3-diphenylaziridine **49** (Scheme 3.14).



Scheme 3.14

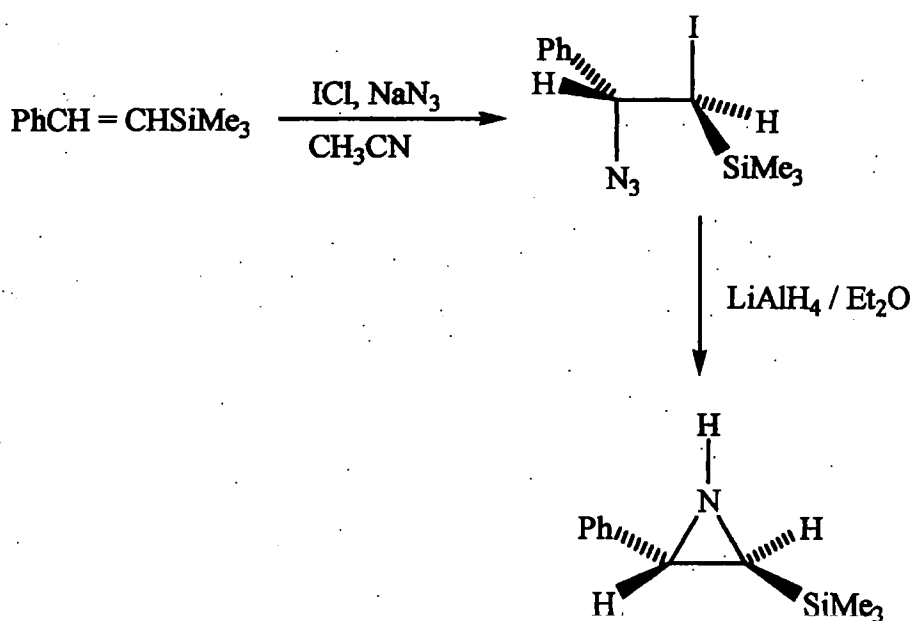
Although, the mechanism of ring closure in the synthesis of silyl-substituted aziridines has not been examined as such, it is assumed it behaves as other ring closures. In one instance

where the preparation of the aziridine could lead to diastereoisomers (Scheme 3.15), the product was found to be stereospecifically *trans*-³⁰.



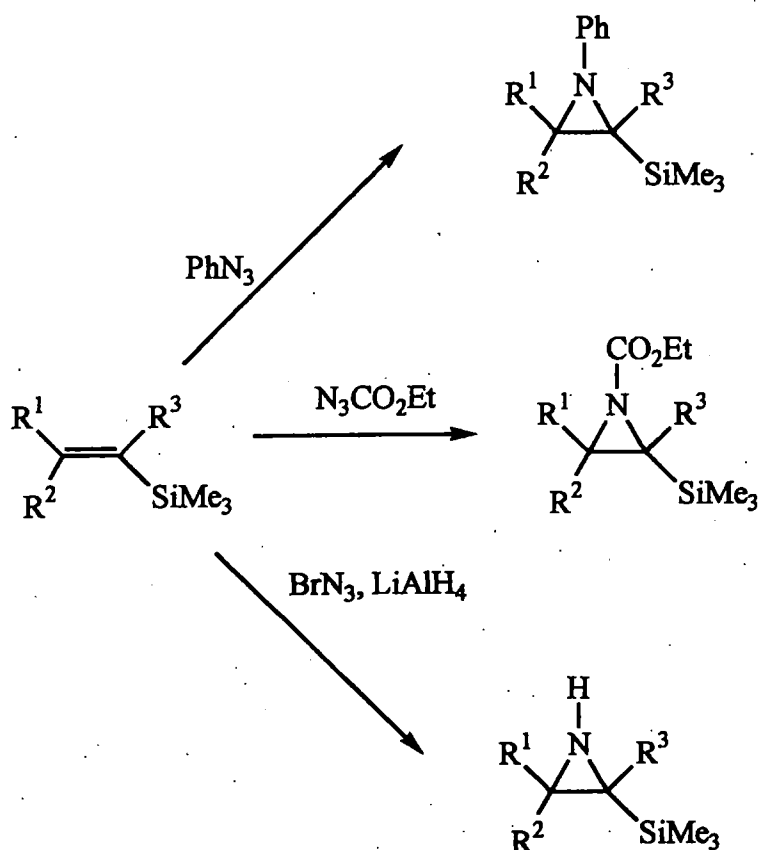
Scheme 3.15

Whilst these workers did not discuss the stereochemistry of formation it would appear that the ring closure proceeds with inversion of configuration as expected. Addition of iodoazide to the *trans*-alkene is expected to undergo an anti-addition to give *erythro* adduct which then leads to the *trans*-aziridine via an $\text{S}_{\text{N}}2$ mechanism (Scheme 3.16).



Scheme 3.16

Kyle³⁶ has synthesised a series of 2-trialkylsilylaziridines by the reaction of vinyl-silanes with organic and halogen azides to give the corresponding silylaziridines (Scheme 3.17).



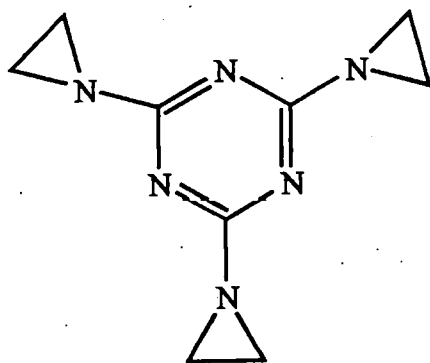
Scheme 3.17

3.5. Some uses of aziridines

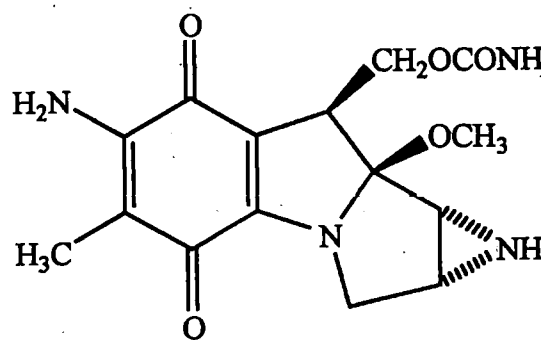
Aziridines and their derivatives have found many applications in industry^{9, 37, 38}. For example, they are used in textiles to produce dyes that are able to resist destruction or removal in hostile environments³⁹. Aziridines have found wide application in plastics, adhesives, lubricants and fuels. Further they are of considerable biological interest⁴⁰. The growing importance of functionalised aziridines in organic synthesis⁴¹ and their presence in bioactive molecules has created a lot of interest among researchers⁴².

They have been found to have mutagenic, carcinogenic, antimicrobial, herbicidal, insecticidal, and anti radiation properties. They owe their activity to the strain of the three-membered ring which renders the aziridine susceptible to ring-opening reactions with various nucleophiles.

Aziridine drugs, such as the anti-cancer nitrogen mustard **50** and antibiotic mytomycin C **51**⁴³ are believed to cross-link the two strands of the helix of DNA by alkylating the nucleophilic groups on the purine and pyrimidine bases, hence interrupting cell-division.



(50)



(51)

Since silyl-substituted aziridines, especially those containing β -trialkylsilyl groups, are relatively new and few of these systems have been studied, little is known of their chemistry. The work covered in this chapter is concerned with :

- (i) The synthesis of β -trialkylsilyl aziridines (Section 3.6.1-3.6.3).
- (ii) The ring preserving reactions of β -trialkylsilyl aziridines (Section 3.6.4).
- (iii) In our efforts to further understand the chemistry of the precursors used for the synthesis of these aziridines, we undertook a study to investigate the ability of a silicon to stabilize a positive charge in the α or β position (Section 3.7)
- (iv) Also in this chapter is discussed a novel and facile method for the synthesis of α -trialkylsilylaziridines via the formation of cyclic sulphates and sultones (Section 3.8).

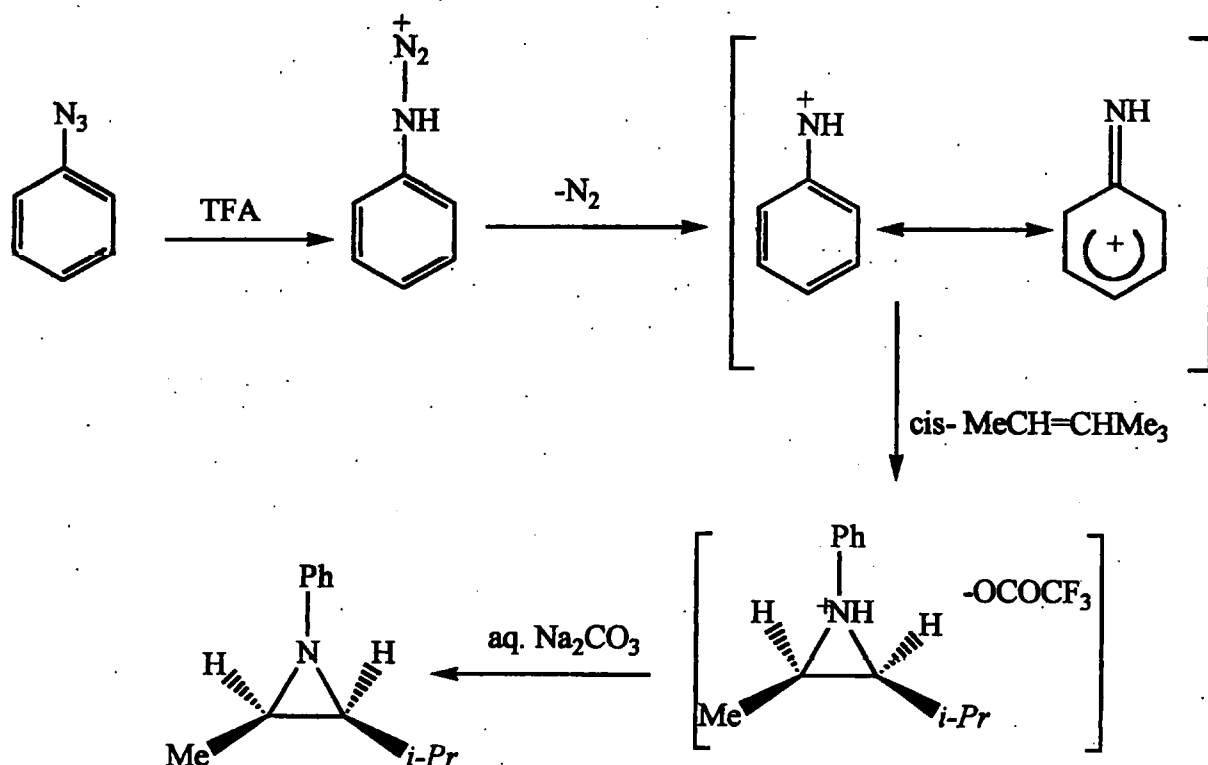
The ring-opening reaction of these silylaziridines is covered in the next chapter.

3.6 Results and discussions

We have extended further the synthetic routes developed by Soobramanien and Kyle to include the synthesis β -silylaziridines from the corresponding allyltrimethylsilanes. Unlike the corresponding β -silylepoxydes⁴⁴, we were able to isolate these compounds.

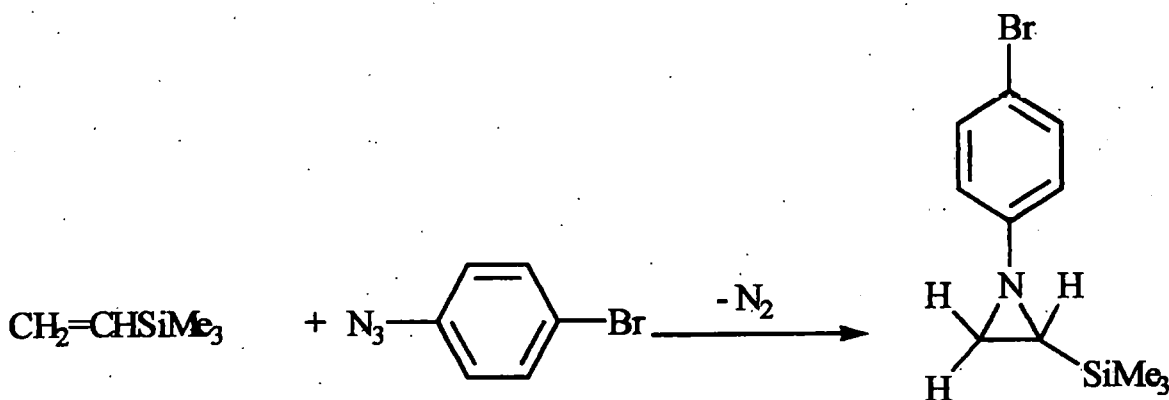
3.6.1 Synthesis of silyl-substituted aziridines from phenylazide by the thermolytic method.

Organic azides such as phenyl azides and benzyl azides have been reported to react thermally with alkenes to give the corresponding aziridines. Takeuchi and his co-workers, recently reported the synthesis of 1-phenyl-2-methyl-3-isopropylaziridine by the reaction of phenylazide and *cis*-4-methylpent-2-ene in the presence of trifluoro acetic acid⁴⁵



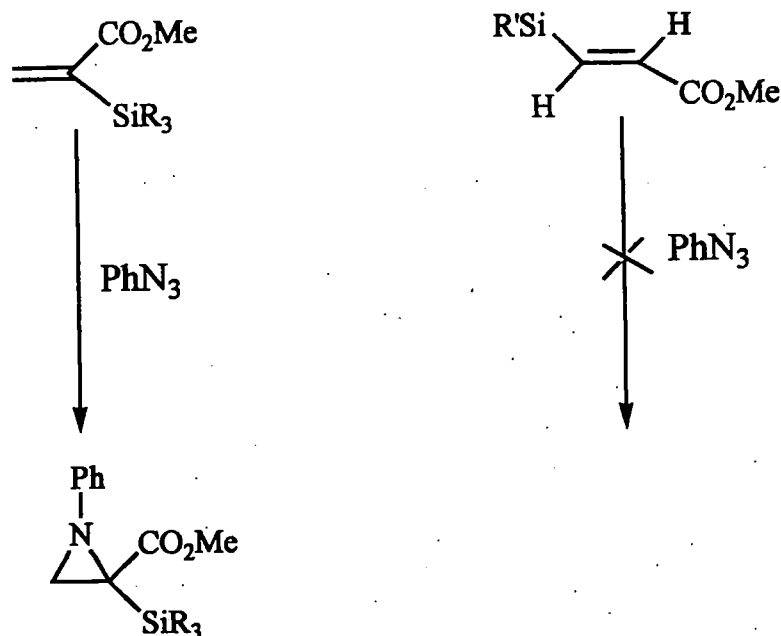
Scheme 3.18

The phenyl azide decomposes in trifluoroacetic acid via its conjugate acid, forming a phenylnitrenium ion. On reaction with the alkene, this leads to the desired aziridine. When Andrianov used the Takeuchi method using phenyl azide, vinyltrimethylsilane and trifluoroacetic acid in hexane at room temperature, a blue black tarry suspension was obtained from which no aziridine was isolated. However, when a mixture of phenyl azide and vinyltrimethylsilane in hexane was heated under reflux for 3½ hours without trifluoroacetic acid, he obtained 1-phenyl-2-trimethylsilyl aziridine²⁷. An analogous compound, *p*-bromophenyl-2-trimethylsilyl aziridine was obtained using thermolysis by Brook in 55% yield (Scheme 3.19)²⁹



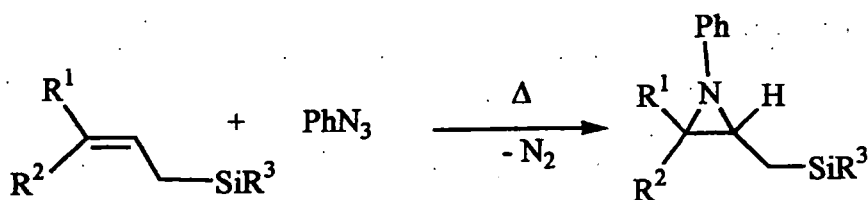
Scheme 3.19

Kyle³⁶ has synthesised various silylaziridines using the thermal reaction of vinyltrimethylsilane with a selection of azides including phenyl, *para*-nitrophenyl and *para*-chlorophenyl. She observed that in most cases only the terminal alkenes reacted to give the corresponding aziridines (Scheme 3.20).



Scheme 3.20

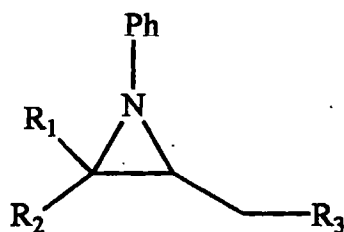
Our work involved the reaction between an equimolar amount of allyltrimethylsilane with phenyl azide under reflux (neat at 90°C) for 10 hours. The crude product was purified by distillation at reduced pressure. The general equation for the formation of the silyl-substituted aziridines from allylsilanes is shown in Scheme 3.21 below.



Scheme 3.21

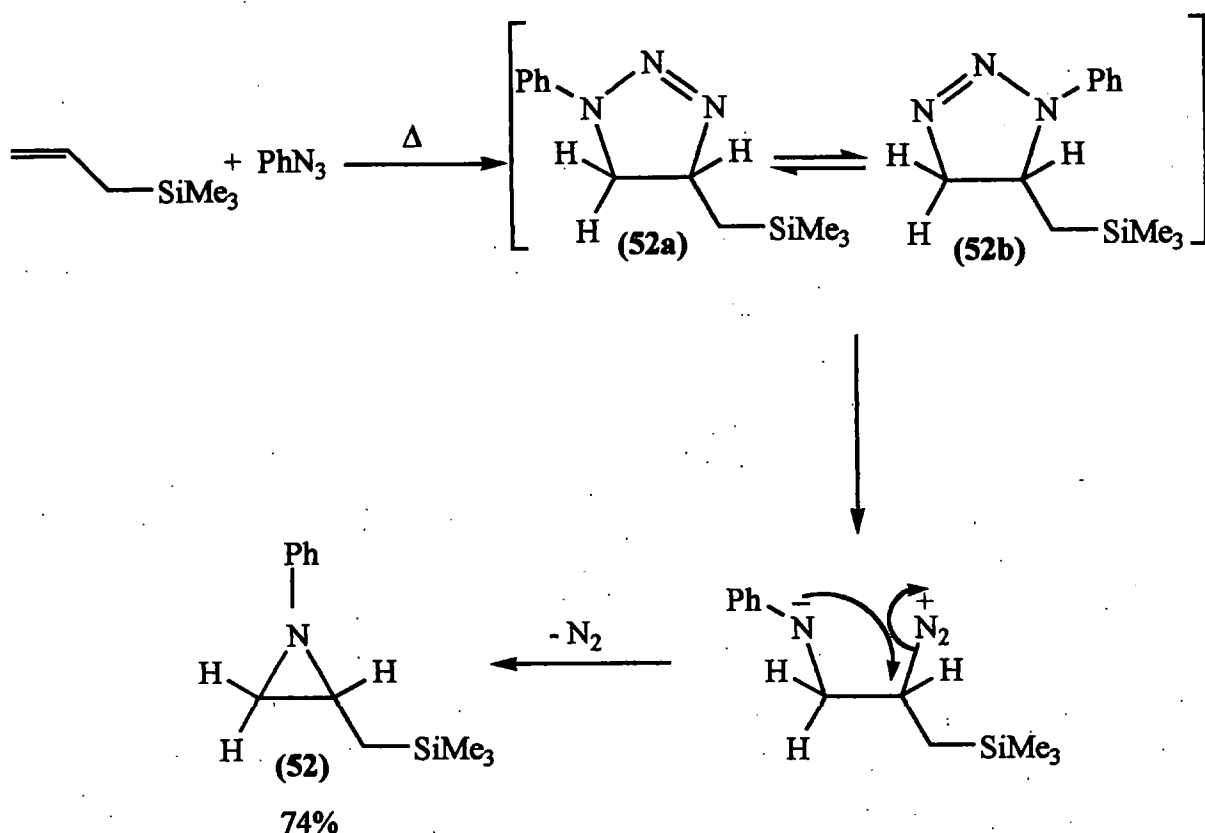
A summary of the silylaziridines formed in this way is given in Table 3.2.

Table 3.2. Silylaziridines obtained from the reaction of phenyl azide with allylsilanes by thermolysis:



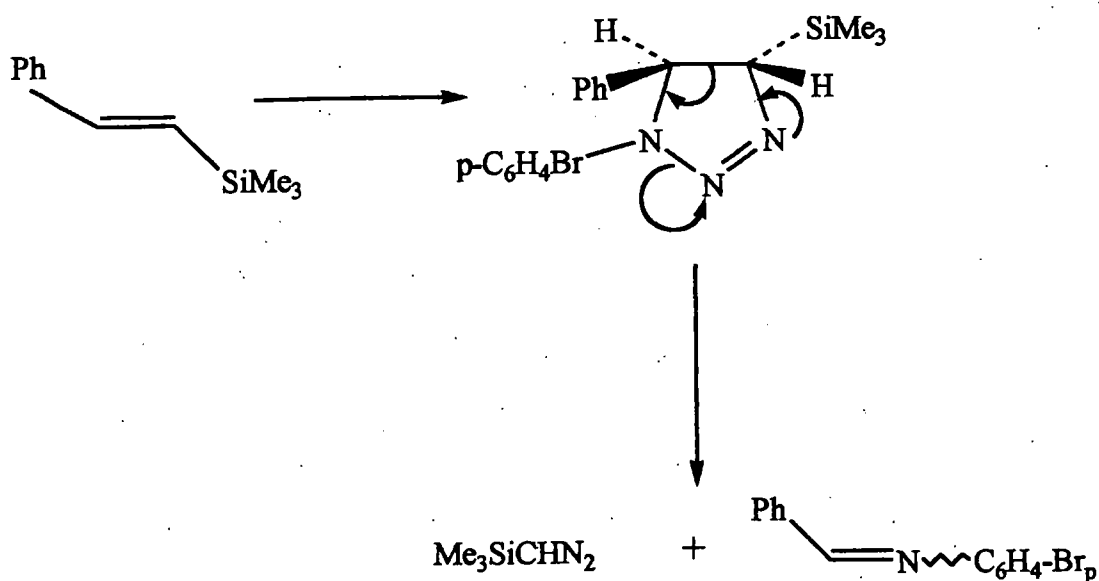
Aziridine	Alkene			(% yield)
	R ₁	R ₂	R ₃	
52	H	H	SiMe ₃	74
53	H	<i>cis</i> -pentyl	SiMe ₃	77
54	Ph	H	SiMe ₃	no reaction.
55	H	H	SiMe ₂ Ph	55
56	H	H	SiPh ₃	51

The mechanism of formation of these aziridines in the absence of trifluoroacetic acid is best explained as involving triazoline intermediates such as **52a** and **52b** (Scheme 3.22). Cycloaddition reactions are known to be very sensitive to steric influences, such that isomer (**52a**) is likely to be preferred.



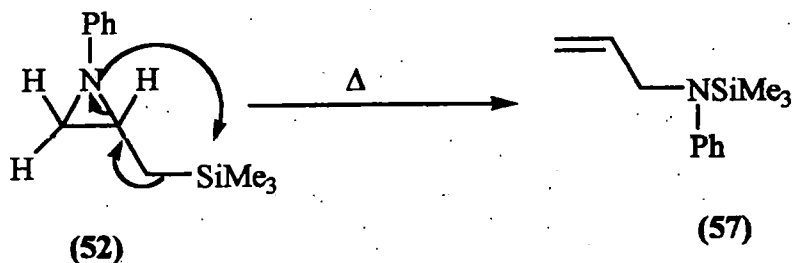
Scheme 3.22

With *trans*-2-phenyl-1-methyltrimethylsilylprop-1-ene, we did not observe any reaction with phenylazide to form aziridine, even at high temperatures ($>100^\circ\text{C}$). This might be due to steric hindrance. It has been observed that cycloaddition reactions of azides with alkenes to give triazolines fail when sterically hindered by substituents⁴⁶. However with *cis*-2-pentyl-1-methyltrimethylsilylprop-1-ene, the reaction was relatively fast, proceeding well even at lower temperatures. Similarly, no aziridine formation was observed by Kyle³⁶ when she reacted *trans*-trimethyl silylstyrene with *para*-bromophenyl azide, instead an enamine was formed, Scheme 3.23.



Scheme 3.23

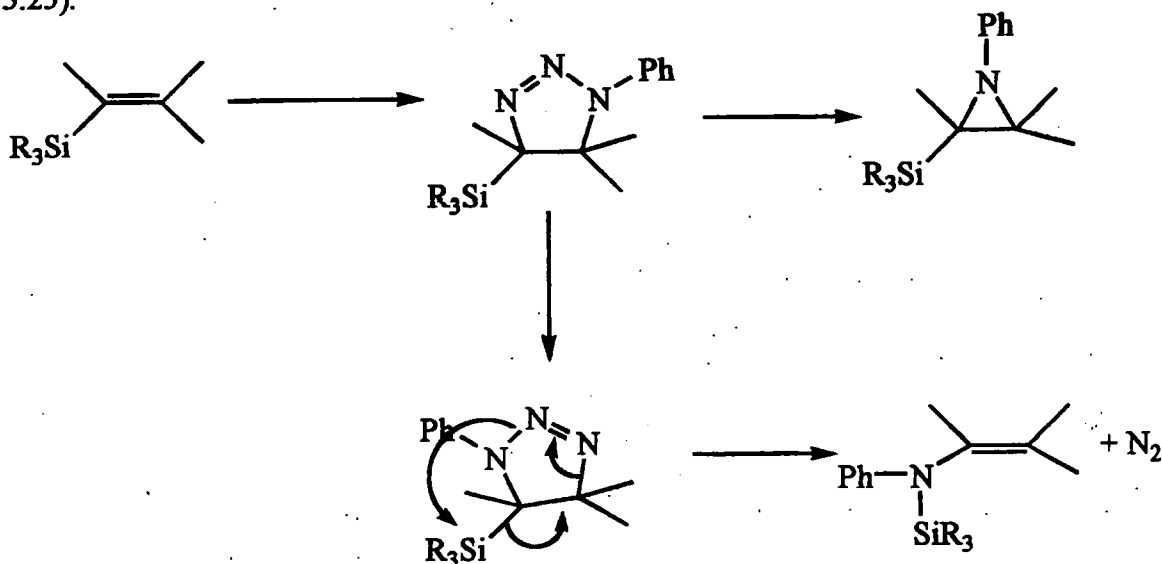
Distillation of the aziridine **52** at high temperature caused it to rearrange to the silylamine **57**, possibly by way of a 1,3 silyl migration (Scheme 3.24)



Scheme 3.24

Aziridines derived from vinylsilanes did not show any tendency towards rearrangement and unlike those derived from allylsilanes, silica gel can be used for their purification without any decomposition. However, small amounts of silylenamines have been detected during the formation of α silylaziridines. Since no aziridine rearrangement occurs, the

enamine was concluded to have arisen from the rearrangement of the triazoline⁴⁷ (Scheme 3.25).

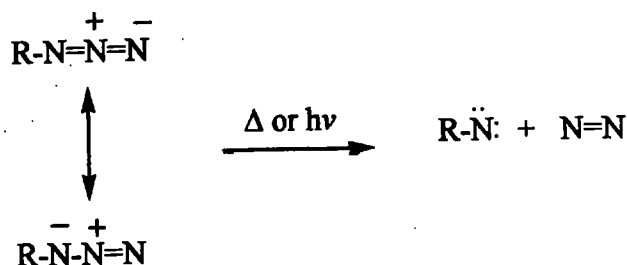


Scheme 3.25

3.6.2 Synthesis of silyl-substituted aziridines from azidoformate by photolytic methods.

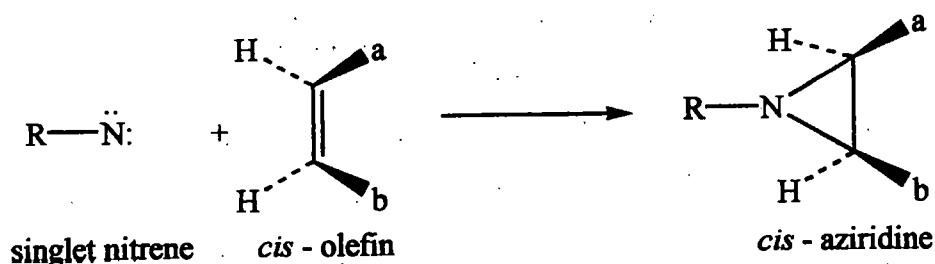
It has been shown that benzenesulfonyl azide⁴⁸ ethoxycarbonyl azide⁴⁹ and benzoyl azide⁵⁰ add to olefins under the influence of light to give aziridines which have the same *cis* or *trans* configuration as the original olefin. This formation of aziridines has been shown to by-pass a triazoline intermediate and occur via a nitrene. This is an uncharged monovalent nitrogen intermediate⁵¹. Nitrenes contain an electron-deficient nitrogen atom having a sextet of electrons in its outer shell.

Theoretically, these species may exist either in the triplet diradical state or in the singlet state, in which the electron-deficient nitrogen is highly electrophilic. Formation of a nitrene is shown in Scheme 3.26



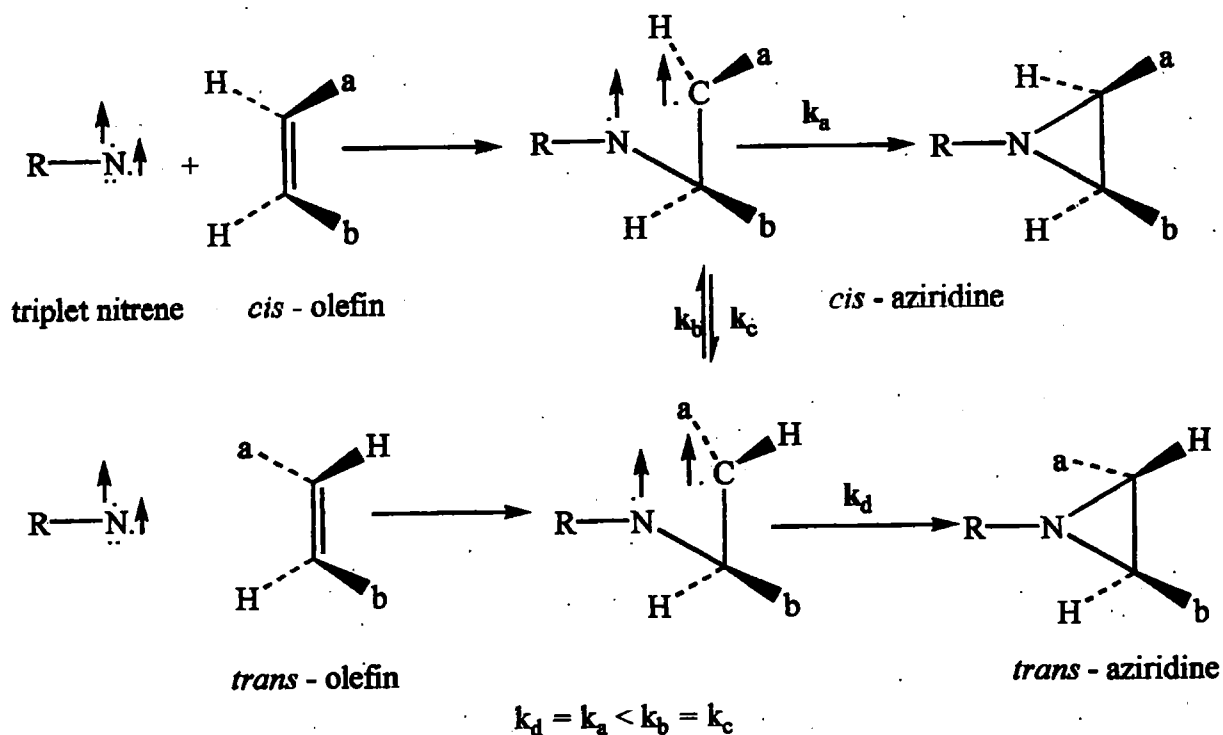
Scheme 3.26

Many investigators⁵² have suggested that the stereospecific addition of such a nitrogen species is generally interpreted as indicating the reaction of a singlet state nitrene, which adds in a single step (Scheme 3.27).



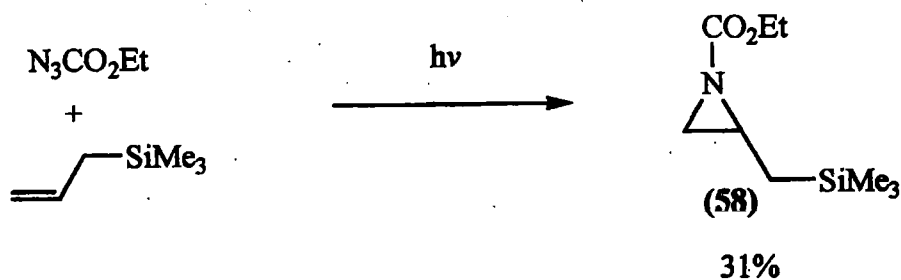
Scheme 3.27

In contrast a non-stereospecific addition indicates a triplet state addition. Such an addition occurs in two discrete steps, via a triplet 1,3-diradical intermediate. The rate of ring closure of the latter is thought to be considerably slower than that for rotation about the C-C bond between the two former olefin carbons. Consequently, stereospecificity is lost and a mixture of *cis* and *trans* aziridine are formed (Scheme 3.28).



Scheme 3.28

In our typical photolytic reaction, an equimolar amount of ethyl azidoformate was added to various allylsilanes in a quartz tube and irradiated for 8 days. High vacuum distillation of the crude product gave N-carboethoxysilyl aziridines accompanied by unidentified polymeric material. The reaction of allyltrimethylsilane with ethylazidoformate to give 1-carboethoxy-2-trimethylsilylmethyl aziridine **58** was the most facile and is representative (Scheme 3.29).



Scheme 3.29

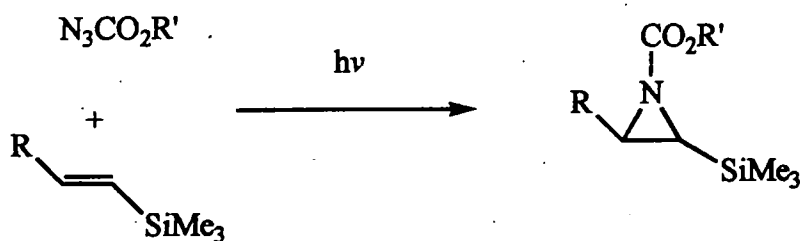
The product of this reaction has already been synthesized by Lukevics³² but our method is more facile (one pot) and has a higher yield.

It is possible that the photolytic reaction could occur by one of three pathways:

- (i) an initial thermal addition of azide to give the triazoline, followed by photochemical decomposition to yield the aziridine;
- (ii) photochemical addition of azide to give triazoline, followed by photochemical decomposition to yield the aziridine;
- (iii) photochemical generation of a nitrene followed by reaction with alkene to give the aziridine.

From the NMR of the reaction mixtures taken at intervals, we observed no signals due to triazolines. Hence, as earlier observed with non silylated systems, the silylaziridines are most likely formed by way of a nitrene intermediate. The following alkenes were used to prepare aziridines by this route: allyldimethylphenylsilane, allyltriphenylsilane, *cis*-1-trimethylsilyloct-2-ene and *trans*-1-phenyl-3-trimethylsilylpropene.

The reaction with allyltriphenylsilane was carried out in carbon tetrachloride, and no signals due to aziridine were observed. Similarly no reaction was observed with *trans*-1-phenyl-3-trimethylsilylpropene. However, allyldimethylsilane and 1-trimethylsilyloct-2-ene did react to form the aziridine (as shown by nmr). However, isolation by either distillation or flash chromatography (on either neutral alumina or silica gel) led to decomposition. In contrast, Kyle³⁶ reacted a number of functionalised vinylsilanes with alkyl-azidoformates to form a wide variety of new silyl aziridines, which she was able to purify by column chromatography over silica gel without decomposition (Scheme 3.30)



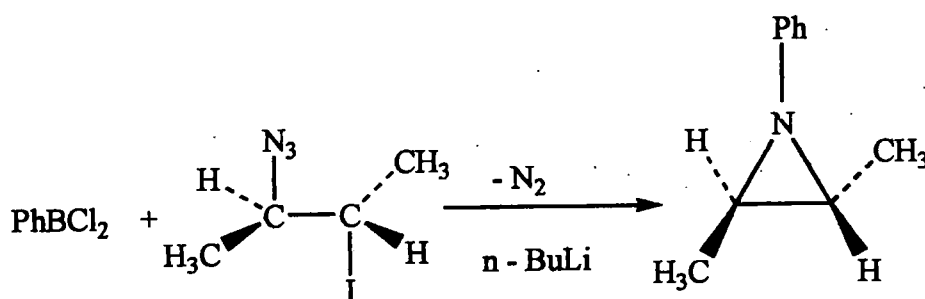
Scheme 3.30

The increased susceptibility of β silylaziridines to decomposition compared to the α silylaziridines is a consequence of the ability of the β C-Si bond to be coplanar with the C-N bond at all times during reaction, thus stabilising any carbenium ion character. Such an overlap is not possible with α C-Si bond.

The N-carboethoxy derivative seems to decompose faster than the N-phenyl derivatives as a result of the increased leaving group ability.

3.6.3 Lithium aluminium hydride reduction of bromo azides.

Lithium aluminium hydride reduction of halogeno azides derived from vinyl silanes has already been shown to lead stereoselectivity to the corresponding N-unsubstituted aziridine (Schemes 3.15 and 3.16). Recently, it has been reported by Brown et al⁵³ that reaction of 2-iodoalkyl azides with organoboranes and the subsequent treatment of the intermediates with base leads stereospecifically to N-substituted aziridines (Scheme 3.31).

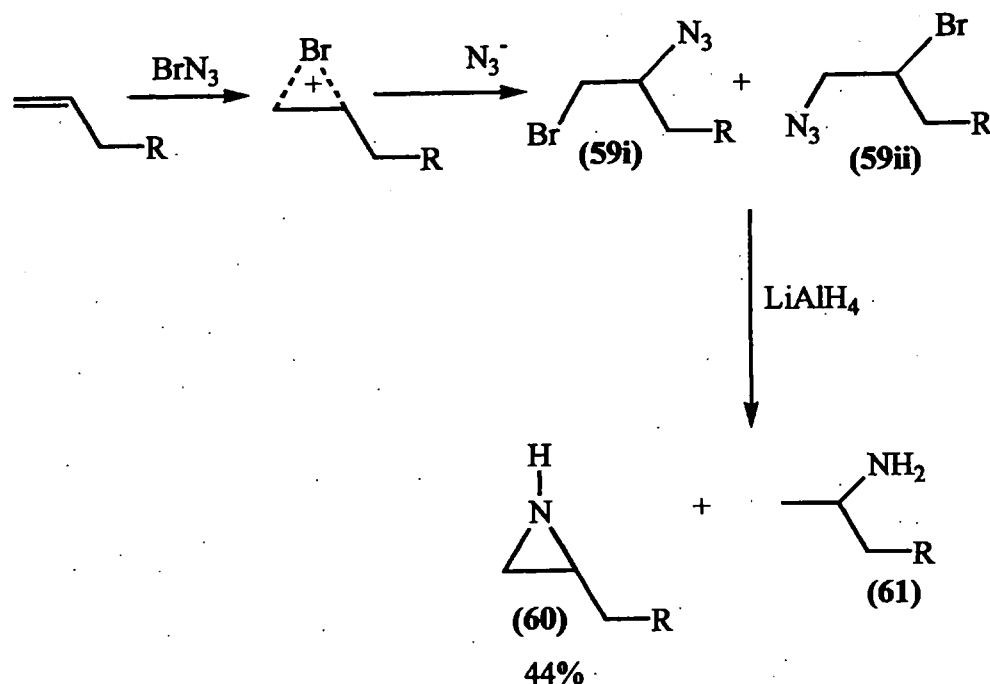


Scheme 3.31

To develop a route to N-unsubstituted and N-substituted, β -silylaziridines, we examined the reaction between halogen azide precursors and lithium aluminium hydride.

To prepare the aziridines, we reacted cold bromine azide, formed from the reaction of sodium azide and bromine in dichloromethane, with allylsilanes at -10°C to give the

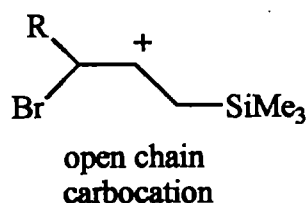
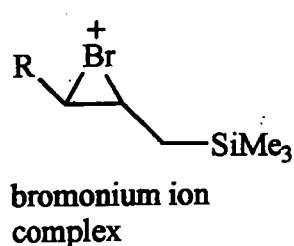
intermediate bromine azide **59** in variable yields (50–95% depending on R). Reduction of 0.015mole of the azide **59** using lithium aluminium hydride(0.043moles) in dry ether at 0° C gave a colourless oil, which was found to be a mixture of the required aziridine **60** and the amine **61**. Any attempt to separate the mixture by flash chromatography led to decomposition of the aziridine to products that we could not identify (Scheme 3.32).



Where R =(a) SiMe₃ (b) SiMe₂Ph (c) SiPh₃

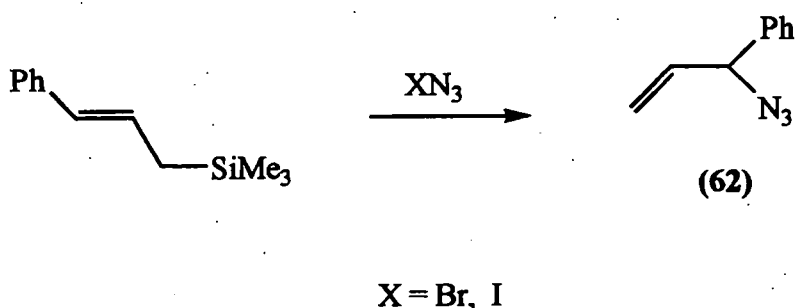
Scheme 3.32

The formation of the bromine azide adduct **59** occurs via a cyclic bromonium ion, which is formed when bromine azide adds to olefins⁴⁵. Nucleophilic attack by azide ion, can occur at both β and γ -carbon resulting into two isomers **59i** and **59ii**. Proton Nmr of the crude mixture showed only signals due to **59i**, this is not surprising as this is the result of nucleophilic attack at the potentially more stable carbocation, that β to the silicon.



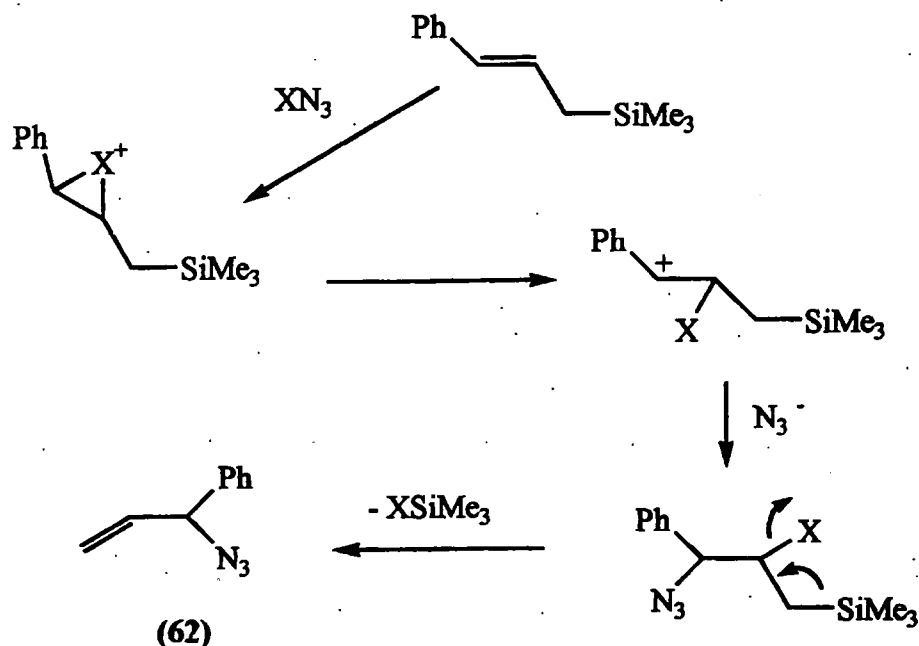
Subsequent reduction of the bromine azide adduct by lithium aluminium hydride gave a mixture of the aziridine **60** and the amine **61**.

To examine the stereochemistry of the intermediate azide and consequently the aziridine formed, we reacted substituted allylsilanes with halogen azides. On reacting bromine azide or iodoazide with *trans*-2-phenyl-1-methyltrimethylsilylprop-1-ene, we were unable to isolate the azido intermediate, hence could not obtain any aziridine. The reaction gave only the allylazide **62** (Scheme 3.33).



Scheme 3.33

A possible explanation for the formation of allylazide **62** is that the phenyl group stabilises the cationic intermediate to a larger extent than the silicon. The azide group then adds to the γ -carbon. The subsequent loss of the trialkylsilyl group gives the allylazide (Scheme 3.34).



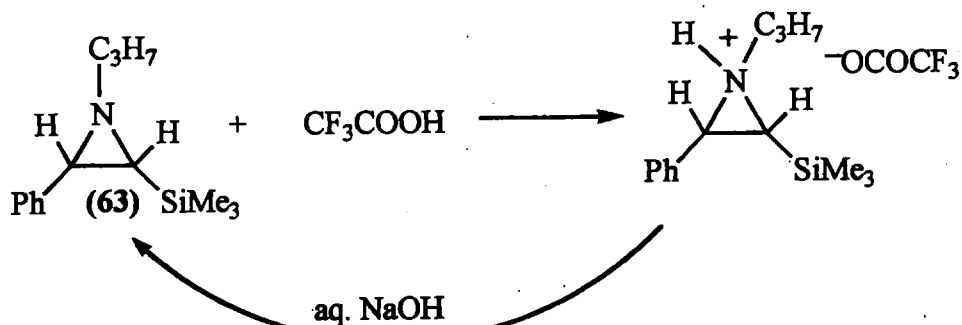
Scheme 3.34

Kyle has also used this method to synthesise silylaziridines (Scheme 3.17). Despite decomposition, our yields of isolatable aziridines (44%) were slightly higher than hers (39%). In a similar fashion, she also observed the formation of amino silanes, during the reduction of bromine azides with lithium aluminium hydride. She also examined the use of different reagents such as K-Selectride®, sodium borohydride, calcium hydride and triphenylphosphine in the last step.

3.6.4 Modification of silyl-substituted aziridines

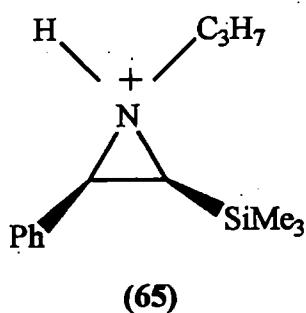
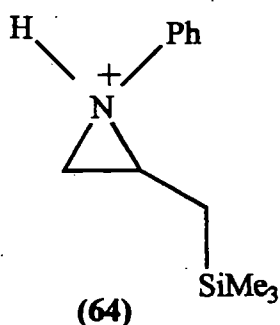
This section describes the ring-preserving reactions of silyl-substituted aziridines, resulting in the modification of the original aziridine. It has been shown, that *cis*-1-propyl-2-trimethylsilyl-3-phenylaziridine **63** can undergo protonation to form an isolatable aziridinium salt with the ring intact³³. On treatment of the salt with aqueous sodium

hydroxide, the aziridine was recovered quantitatively (Scheme 3.35). A similar protonation reaction of 1-phenyl-2-trimethylsilylmethylaziridine did not give an isolatable aziridinium salt, but gave a ring-opened product (more details in chapter four).



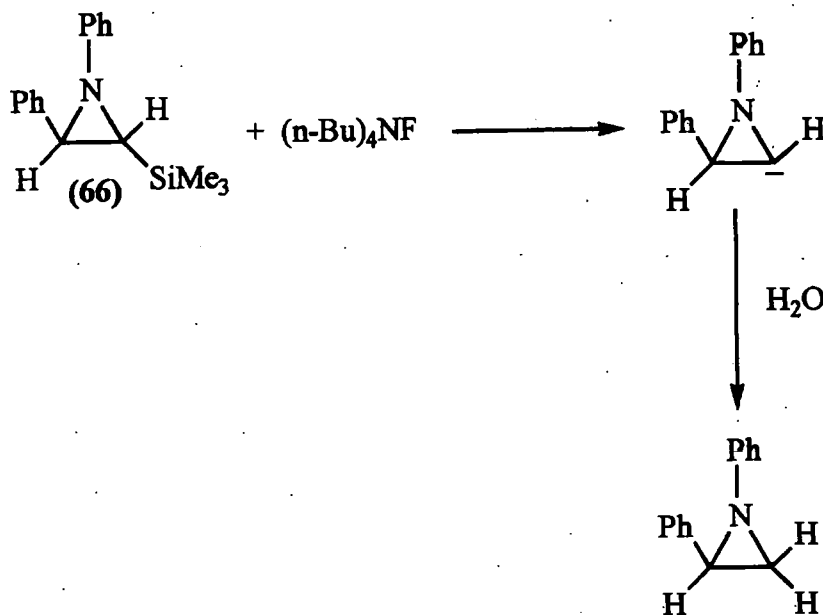
Scheme 3.35

A possible explanation for this is that with the protonation of 1-phenyl-2-trimethylsilylmethyl-aziridine 64 the C-Si bond can be *syn* periplanar with the C-N bond such that on protonation ring cleavage can occur. This is not possible with the protonated intermediate from *cis*-1-propyl-2-trimethylsilyl-3-phenylaziridine 65, because the geometry of the C-Si bond is fixed.



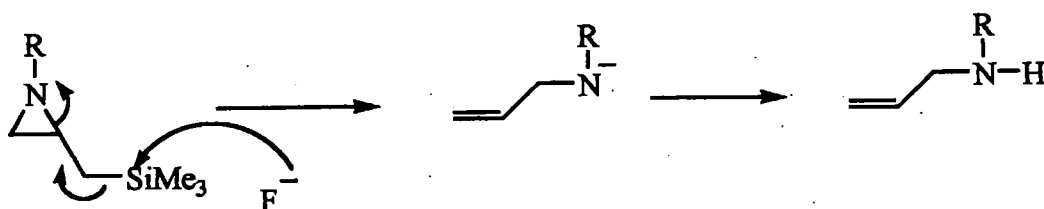
The ability of some silyl-substituted aziridines to undergo fluorodesilylation reactions renders them very useful for further functionalisation, as they form carbanion

intermediates. For instance, fluorodesilylation of *trans*-1-phenyl-2-trimethylsilyl-3-phenylaziridine **66** with tetrabutylammonium fluoride in acetonitrile under reflux for 18hrs gave 1,2-diphenyl aziridine in 70% yield³⁶(Scheme 3.36).



Scheme 3.36

Our efforts to desilylate 2-trimethylsilylmethyl aziridines with the ring intact were unsuccessful, instead ring-opened products were obtained (Scheme 3.37).

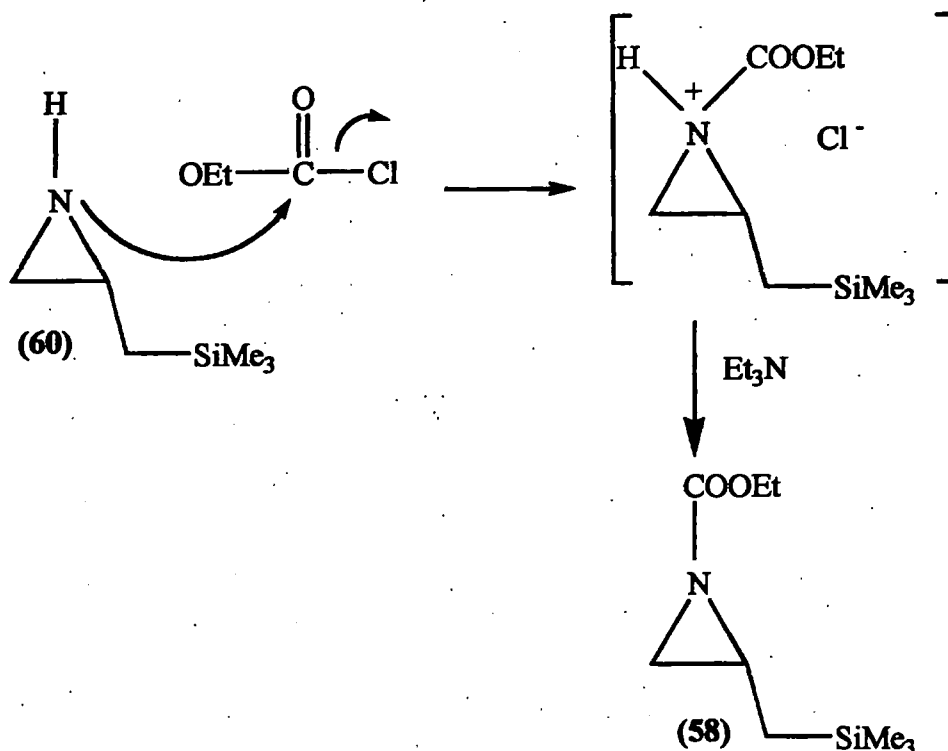


Scheme 3.37

3.6.4.1

Acylation of silyl-substituted aziridines

Acylation of the aziridine nitrogen was achieved using ethylchloroformate in the presence of triethylamine in dry ether. The reaction involves nucleophilic attack by the aziridine nitrogen on the acyl-carbon (Scheme 3.38). The triethylamine is usually employed in large excess such that any acid, which might encourage ring-opening, is removed.

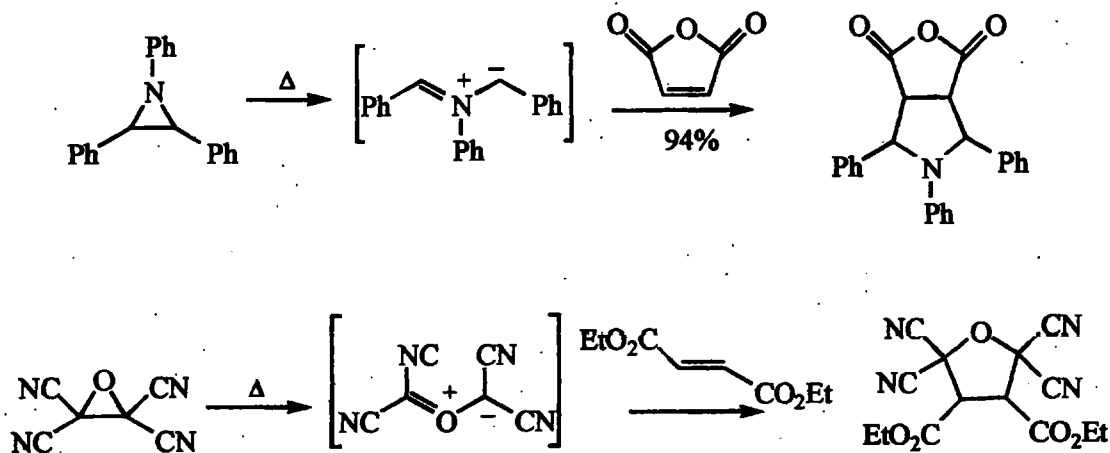


Scheme 3.38

The use of other acylating agents such as acetyl chloride, acetic acid, 2-chloropropyl propiolate, gave black tars which could not be identified.

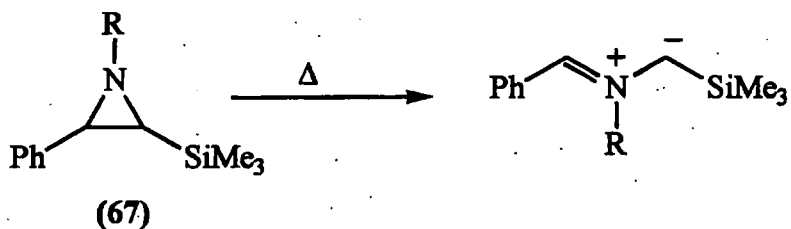
3.6.4.2 Ring expansion of silylaziridines

Aziridines⁵⁴ and epoxides⁵⁵ can undergo cycloaddition reactions with activated alkenes, acetylenes, and aromatic compounds. The aziridine and epoxide rings undergo a C-C bond cleavage to form an ylide intermediate which is a 1,3-dipole (Scheme 3.39)



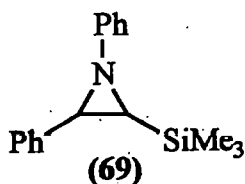
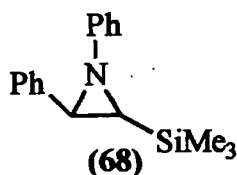
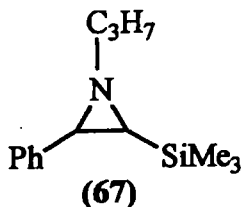
Scheme 3.39

α -silyl aziridines such as **67** might be expected to readily form 1,3 dipoles, as a result of stabilization by the adjacent silicon (Scheme 3.40).



Scheme 3.40

In an attempt to investigate the cycloaddition reactions of silylated aziridines, we synthesised *cis*-1-propyl-2-trimethylsilyl-3-phenylaziridine **67**, *trans*-1-phenyl-2-trimethylsilyl-3-phenylaziridine **68**, and *cis*-1-phenyl-2-trimethylsilyl-3-phenylaziridine **69** according to literature procedures⁵⁴.



They were reacted with acetylene dicarboxylate, maleic anhydride and diethyl maleate at reflux in toluene. They all reacted to give brown tars which we were unable to analyse.

3.7 Further studies on the ability of a silicon to stabilise a positive charge in the α - or β -position.

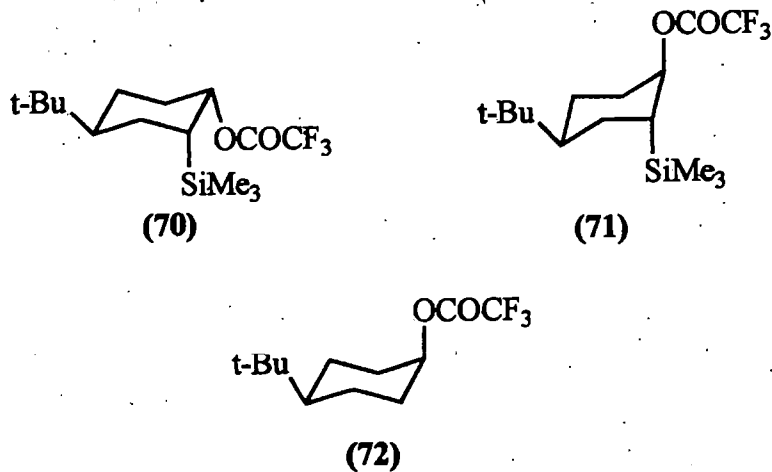
3.7.1. Introduction

Vinyl- and allylsilanes are of considerable theoretical interest from the stand point of the effect of silicon on the chemical behaviour of an olefinic group. The π -electrons of a carbon-carbon double bond is highly polarisable and hence a study of such compounds should provide important information on the electronic effects of silicon in organic synthesis⁵⁶. As discussed earlier, under appropriate conditions, proximate silicon groups can stabilise negative or positive charge and can strongly perturb the π -system in a variety

of molecules. The effect of a silicon atom on the reactivity of a functional group in an attached carbon chain can be explained on the basis of:

- (i) inductive effects, associated with the presence of the silicon atom either α or β to the site of unsaturation.
- (ii) field effects
- (iii) (p-d) π bonding, associated with α substitution and
- (iv) hyperconjugation, which is usually associated with β substitution.

It is worth noting that, a particular property of a silicon compound, or intermediate, is a result of a combination, to a greater or lesser extent, of each of these effects and the particular contribution of one or another effect cannot always readily be disentangled. It has been established beyond doubt that alkyl substituents stabilises carbonium ions and accelerate their formation in ionization processes but in contrast, there seems to be a reluctance for organosilanes to undergo reactions leading to cationic centers α to silicon⁵⁷. In fact, it has been observed by Cartledge and Jones⁵⁸ that $(\text{CH}_3)_3\text{SiC}(\text{CH}_3)_2\text{Br}$ solvolyzes slower than $(\text{CH}_3)_3\text{CC}(\text{CH}_3)_2\text{Br}$. Fleming has shown that the trimethylsilyl group exerts little directing influence on the regioselectivity of cycloaddition reactions⁵⁹. The effect of α -silicon on the stability of vinyl cations has been studied⁶⁰ and shown that α -methyl and α -silyl substituents stabilise vinyl cations to a similar degree. A solvolysis study of the effect of Me_3Si and Me_3C in stabilising vinyl cations was interpreted as indicating that the Me_3C group had a greater stabilising effect than the Me_3Si group⁶¹. Stabilization of cationic centers by β - carbon-metal bonds is known⁶². Although the β -effect has dominated much development in the synthetic usage of organosilicon compounds and has been designated as a powerful effect, the qualitative description of the origin of the β -silicon effect⁶³ is still controversial. Previous mechanistic studies of β -silyl systems focused on open-chain systems, in which the *trans* and *gauche* conformers are in rapid



equilibrium⁶⁴. An attempt to quantify and elucidate the effect of the Me_3Si group on β -carbonium ions was reported by Lambert⁶⁵, who studied the solvolysis of cyclohexyl systems in 97% $\text{CF}_3\text{CH}_2\text{OH}$ and found that they all gave cyclohexene as the only product. It was observed that the *trans* isomer **71**, solvolyzed 2.5×10^6 times faster than **72**, whereas, the *cis* isomer **70**, solvolyzed 3.4×10^4 times faster than **72**. In the *trans* isomer, the Me_3Si group is frozen into the anti-periplanar (diaxial) relationship with respect to the leaving group, due to the *t*-butyl group. This is the ideal conformation for maximal hyperconjugation, whereas in the *cis* isomer, the dihedral angle between the two substituents is around 60° , and a much smaller contribution from hyperconjugation would be expected. Jorgensen and co-workers⁶⁶ explored the origin of β -stabilization and concluded that the effect arises from hyperconjugation.

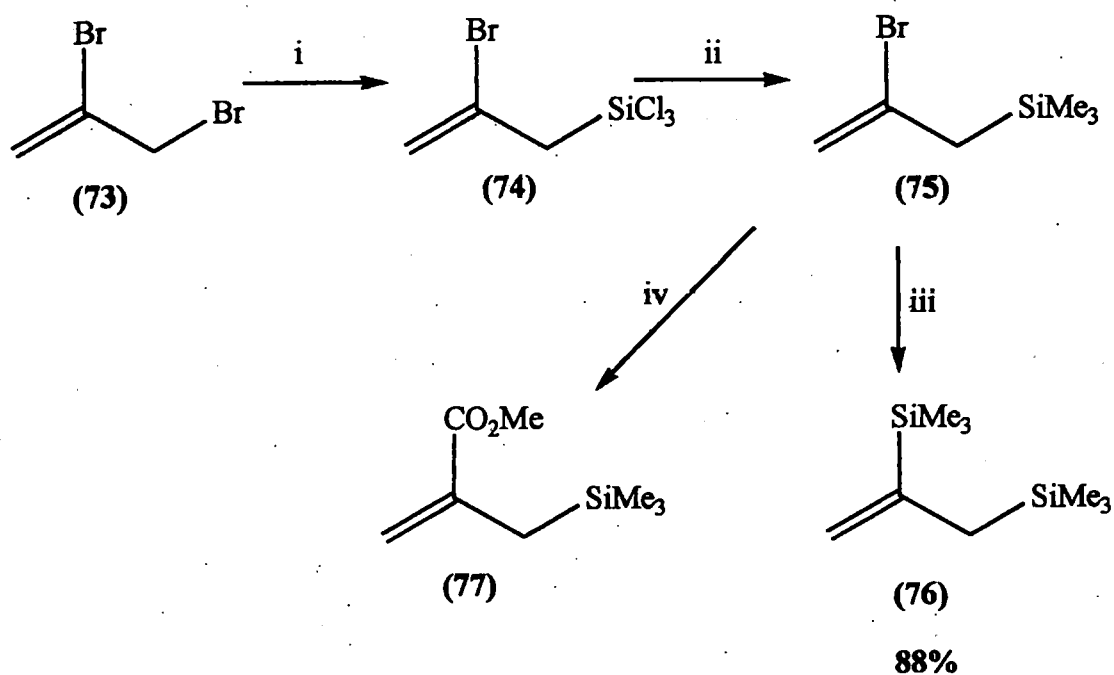
Although the reaction of vinyl- and allylsilanes with various electrophiles is well documented, much less is known about the reaction of compounds that contain both types of functionality. It is generally agreed that allylsilanes are more reactive towards electrophiles than vinylsilanes, but few examples of this phenomenon have been reported with substrates which are simultaneously vinyl- and allyl- silanes⁶⁷. Hence, we wished to examine the ability of silicon to stabilise a positive charge in systems containing both vinyl and allyl groupings. We considered the reaction of the simplest bistrimethylsilyl alkene with electrophiles, where the trimethylsilyl group is the only directing group.

3.7.2. Results and discussion.

We synthesised the bistrimethylsilylalkenes **76** and **79** (Scheme 3.41) and (Scheme 3.42). These are very interesting substrates since they are simultaneously allyl- and vinylsilanes. They were reacted with hydrogen chloride gas and trifluoroacetic acid (TFAc). The pattern of their reactivity was determined by Nmr comparison with authentic samples.

3.7.2.1. Synthesis of 2,3-bistrimethylsilylpropene(**76**)

2,3-bistrimethylsilylpropene **76**, was prepared in three steps. Treatment of commercially available 2,3-dibromopropene **73** with trichlorosilane in the presence of a catalytic amount of cuprous chloride gave the allyltrichlorosilane **74**. The crude trichlorosilane was then added to an ethereal solution of a methyl Grignard reagent to give 2-bromoallyl-trimethylsilane, **75**⁶⁸ (Scheme 3.41). Reacting the bromosilane with *tert*-butyllithium in THF and quenching with chlorotrimethylsilane gave the bistrimethylsilane in 88% yield. The versatility of the 2-bromo-3-trimethylsilylpropene as a synthetic intermediate was demonstrated by its simple conversion to the silyl-acrylate **77**.

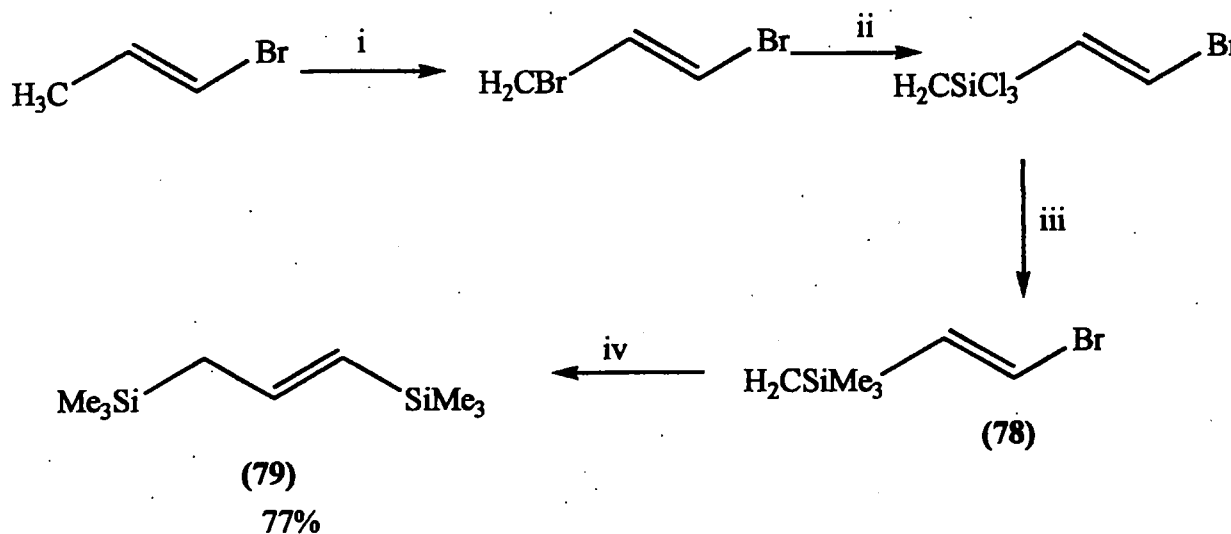


(i) HSiCl_3 , Et_3N / CuCl , Et_2O (ii) 3MeMgI / Et_2O (iii) $t\text{-BuLi}$ / ClSiMe_3
 (iv) $\text{CO}_2(\text{s})$, MeOH/H^+

Scheme 3.41

3.7.2.2 Synthesis of *trans* 1,3-bis(trimethylsilyl)propene(79)

Reaction of the commercially available 1-bromo-1-propene with N-bromosuccinimide (NBS) and a catalytic amount of benzoyl peroxide (BPS) in carbon tetrachloride gave the dibromide, which was then converted into 1-bromo-3-trichlorosilyl-propene⁶⁹(Scheme 3.42). Using similar conditions to those detailed in Scheme 3.41, *trans*-1,3 bistrimethyl silyl propene **79** was isolated in 77% yield.

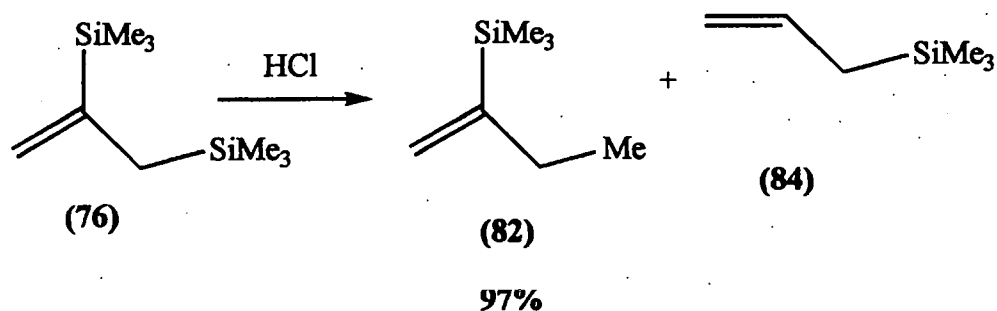


(i) NBS, BPO, reflux (ii) HSiCl_3 , $\text{Et}_3\text{N}/\text{CuCl}$, Et_2O (iii) 3MeMgI
 (iv) $t\text{-BuLi}$, ClSiMe_3

Scheme 3.42

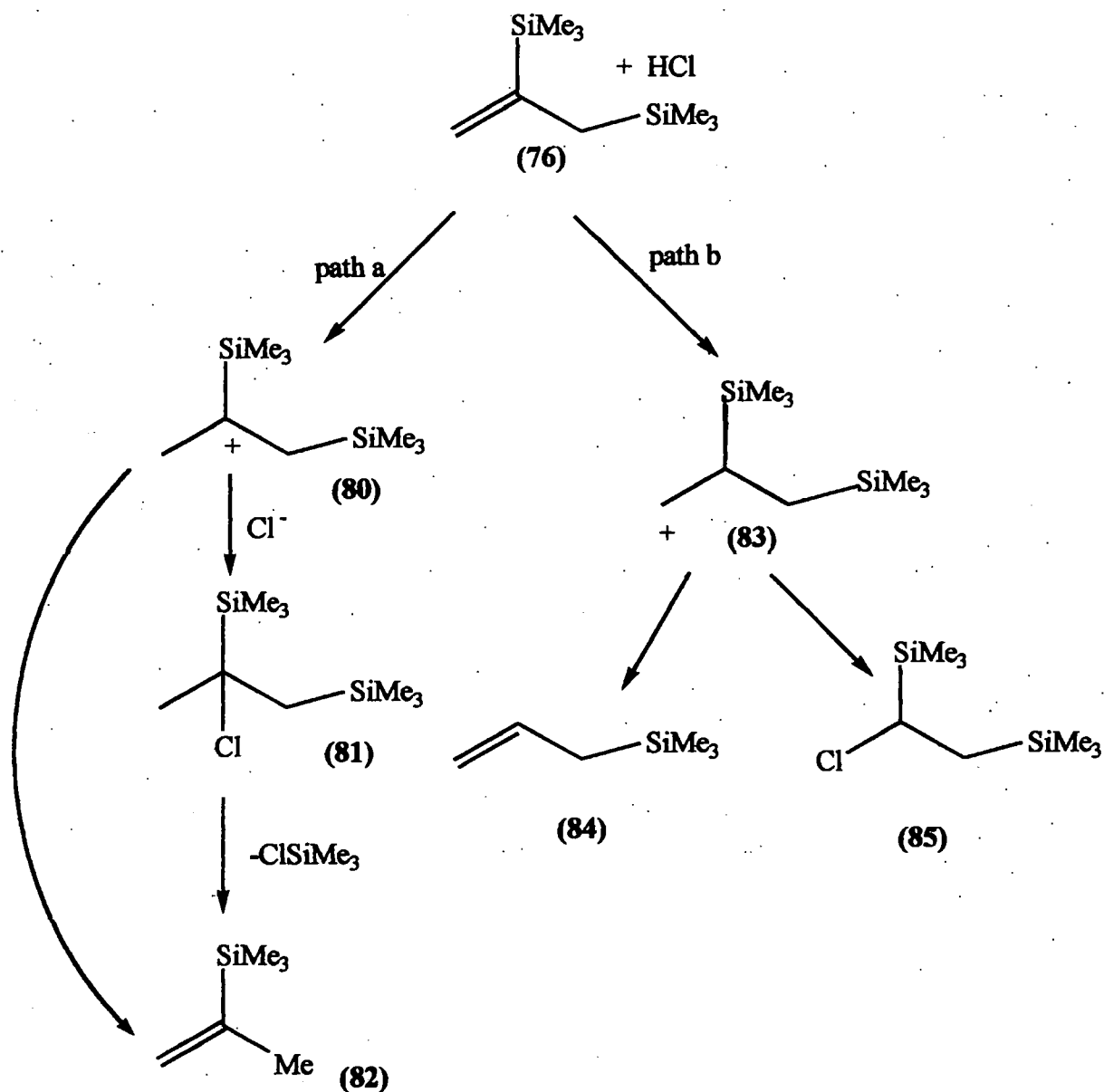
3.7.2.3 Reaction of 2,3-bis(trimethylsilyl)propene with hydrogen chloride gas

Reacting 2,3-bis(trimethylsilyl)propene 76 with hydrogen chloride gas, gave a mixture of two products 82 and 84. The ^1H nmr showed that more than 97% of the product was 82 (Scheme 3.43).



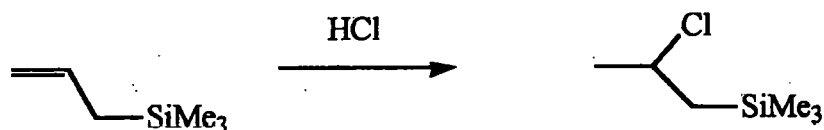
Scheme 3.43

2,3-bistrimethylsilylpropene **76** can react with hydrogen chloride gas solely as a terminal allylsilane (Scheme 3.44, path a) or as a vinylsilane (path b). As an allylsilane, it will form an intermediate β -carbonium ion **80**, which is stabilized by hyperconjugation with the trimethylsilyl group β to the cationic center⁶³. This intermediate might be destabilized by the α silicon. This intermediate can also react further with the chloride to form the addition product **81**, which might subsequently lose trimethylsilyl chloride to give the alkene **82**. Alternatively, **80** can undergo direct substitution to give the same alkene. Alternatively, **80** can undergo direct substitution to give the same alkene.



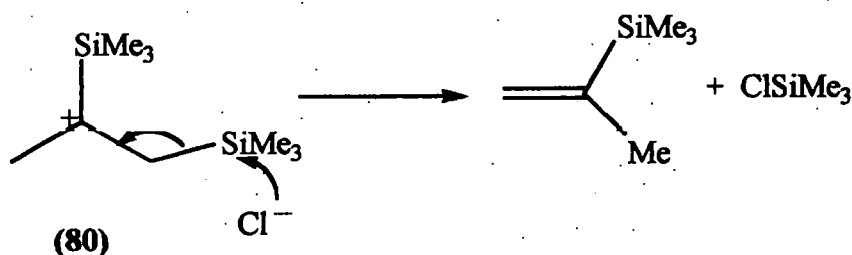
Scheme 3.44

It has been shown that Markownikoff addition takes place when terminal allyltrimethyl silanes are treated with hydrogen chloride⁷⁰ hence supporting the formation of **81**.

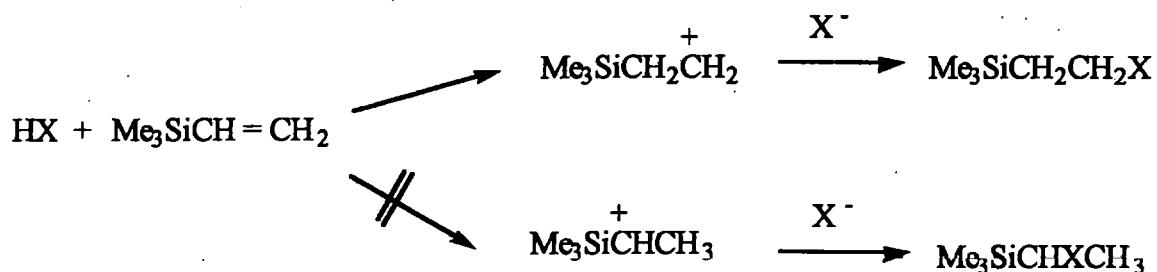


The loss of trimethylsilyl chloride from **81** is in accordance with the observations of other workers^{71, 72}, that a β -silicon atom strongly activates the departure of other groups under both solvolytic and pyrolytic conditions.

The formation of alkene **82** directly from carbocation **80** is a result of it undergoing cleavage involving electron release from silicon to the electron deficient β -carbon. The formation of a "siliconium ion" is avoided by simultaneous or prior union with the chloride ion. This is a direct consequence of the electropositive nature of silicon as compared to carbon.

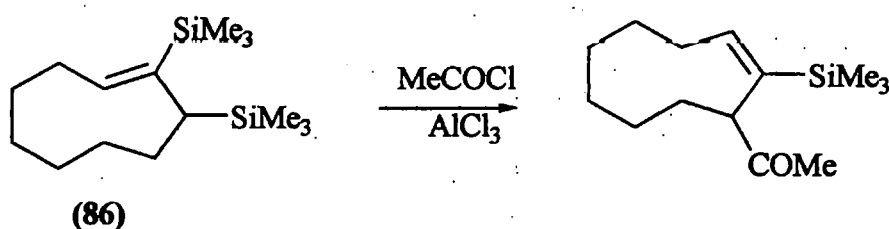


Alternatively, **76** can react as a vinylsilane (path b) to form the carbonium ion intermediate **83** which is still stabilized by a β -silicon. Nucleophilic substitution of the trimethylsilyl group β to the positive charge can occur to give the allylsilane **84** or addition to the intermediate can occur to give **85** which will subsequently lose trimethylsilyl chloride to give **84**. The possibility of formation of the primary carbocation **83** is an indication of the non-inductive electrical effects of the trimethylsilyl group⁷³. An example of this "anomaly" is the anti-Markownikoff addition of hydrogen halides under ionic conditions to vinylsilanes⁷⁴ (Scheme 3.45).



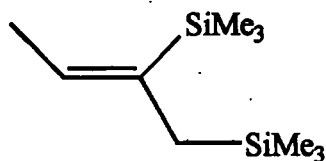
Scheme 3.45

This observation was rationalised in terms of hyperconjugation of the primary carbonium ion with the β silyl substituent. The stabilization of primary carbonium ion **83** by hyperconjugation is only possible after rotation of the C-Si bond, through 90° . With the allylsilane (via path a), the C-Si bond is already in the same plane as the π orbital of the C-C double bond, therefore it will be able to stabilise the developing positive charge throughout the electrophilic addition reaction. Dunogues⁷⁵ has also shown that molecules that are both vinyl- and allylsilanes, such as **86**, prefer to react as an allylsilane (Scheme 3.46).

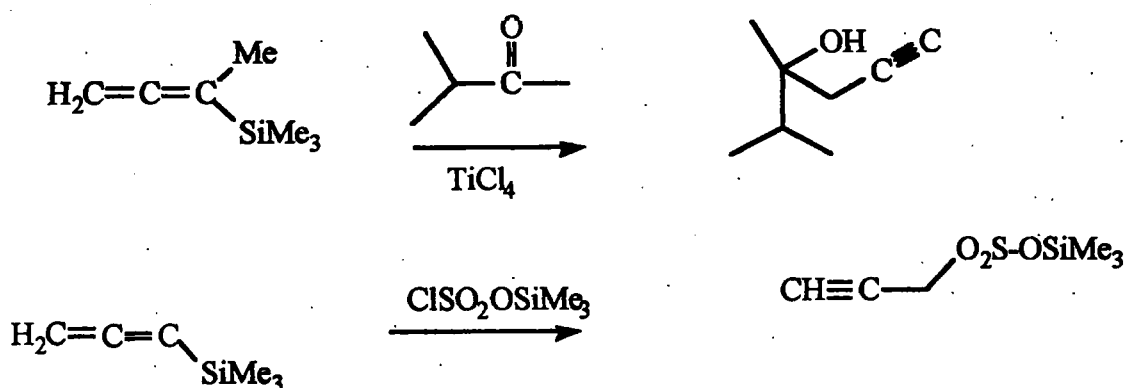


Scheme 3.46

At first, system **86** appears a fairer test of vinylsilane versus allylsilane reactivity since the potential carbonium ion are both secondary with respect to the number of carbons attached. However, conformational effect may prevent hyperconjugation during reaction and



therefore bias the relative reactivities. Perhaps a better system could be the silane shown below, prepared from 1,2-dibromobut-2-ene, however this was not commercially available. It has also been shown that allenylsilanes can act as vinyl or allylsilanes. In general, allylsilane behaviour dominates over vinylsilane behaviour^{76,77,78}(Scheme 3.47).

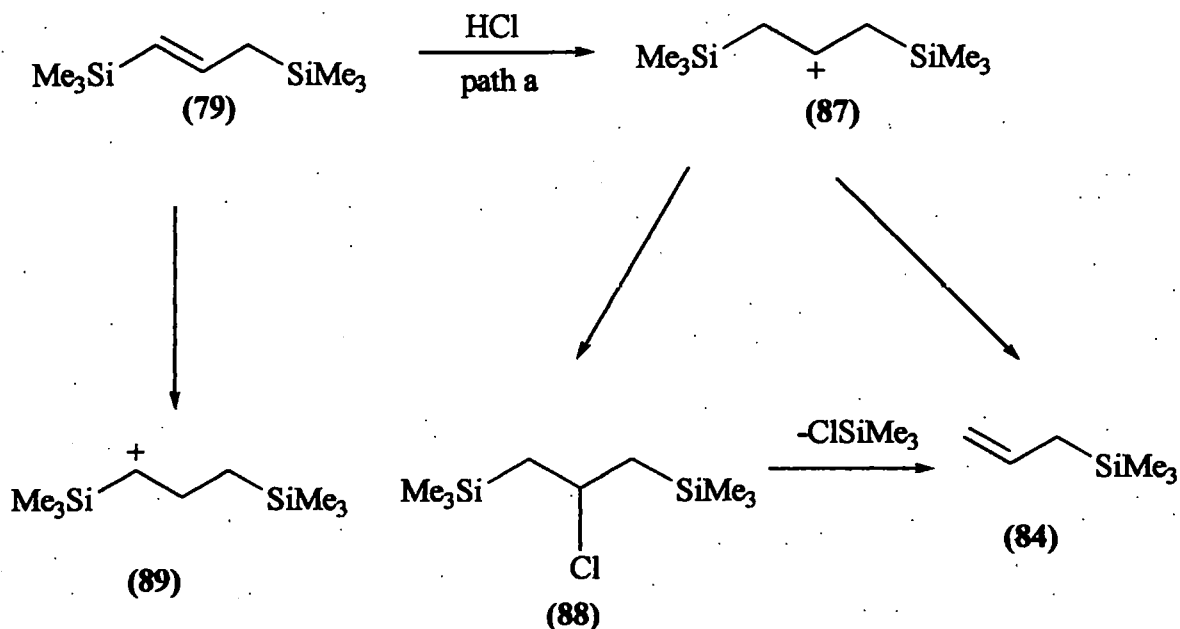


Scheme 3.47

The above observation is in accord with overlap considerations, the C-Si bond of the alkenylsilane being coplanar with the allylic π -bond. A similar reaction pattern was observed when we reacted 2,3-bis(trimethylsilyl)propene **76** with trifluoroacetic acid.

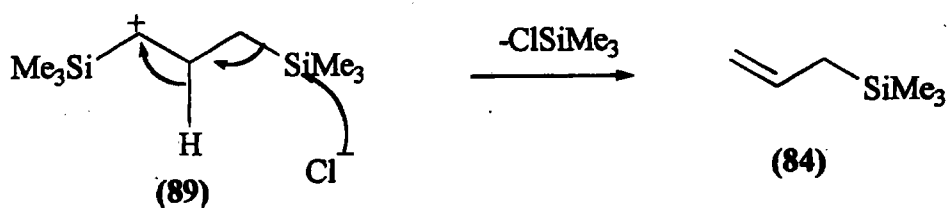
3.7.2.4 Reaction of 1,3-bistrimethylsilylpropene with hydrogen chloride.

We also observed that reaction of 1,3-bistrimethylsilylpropene **79** with hydrogen chloride gas or trifluoroacetic acid gave predominantly the addition product **87** which subsequently collapsed to form allyltrimethylsilane **84** (path a) (Scheme 3.48).



Scheme 3.48

In this case, the intermediate **87** is favoured by **79** reacting as both a vinyl and an allylsilane. **87** can either undergo nucleophilic addition or substitution to form **88** or **84** respectively. Another possible explanation for the formation of the allyltrimethylsilane **84** from **79** is reaction via path (b) to form the carbocation **89**, which is destabilized by the α silicon but stabilized by the γ -silicon.^{79, 80, 81} Attack at the silicon γ to the carbocation by the chloride ion and a subsequent 1, 2 hydride transfer leads to allyltrimethylsilane **84**, Scheme 3.49. However, this mechanism seems less unlikely.



Scheme 3.49

In conclusion, our observation indicate that in systems containing both allyl- and vinylsilanes, the allyltrimethylsilane reacts preferentially to form an electrophilic substitution product via a β silylcarbonium ion which is stabilized by hyper conjugation. Subsequent β elimination gives the alkene. We can also infer that, the β stabilization is greater than α silicon destabilization.

3.8 Improved and novel synthesis of cyclic sulphates and Sultones: A versatile route to aziridine synthesis.

This section describes in details our efforts to find versatile routes to cyclic sulfates, which have been shown to be good precursors of the corresponding aziridines. Using a slight modification of the synthetic route we developed, we discovered that sultones, could also be prepared using the same reagent.

3.8.1. The chemistry of cyclic sulfates

Cyclic sulfates are vicinally substituted electrophiles⁸². Like epoxides, they have a unique role in organic synthesis; they simultaneously activate and protect adjacent functionalized carbon atoms for nucleophilic attack. They are usually superior to their acyclic counterparts because their cyclic nature renders competing elimination processes stereoelectronically unfavourable⁸³.

The parent ethylene cyclic sulfate has been known since 1932⁸⁴. Kaiser⁸⁵ carried out extensive studies on the structure and reactivity of these cyclic esters and has compared the rates of their hydrolysis with acyclic counterparts. They established that these cyclic sulfates hydrolyze in alkaline medium 10^7 times faster than the corresponding acyclic analogues. X-ray analysis of the parent ethylene sulfate indicates that it exists in a puckered conformation, having an angle of 20.6° between the C-4 and C-5 bond and a O-S-O bond angle of 98.4° which is substantially smaller than the unstrained tetrahedral angle of 109.5° (Figure 3.1)⁸⁶

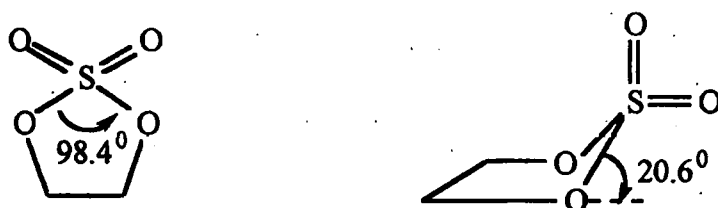


Figure 3.1

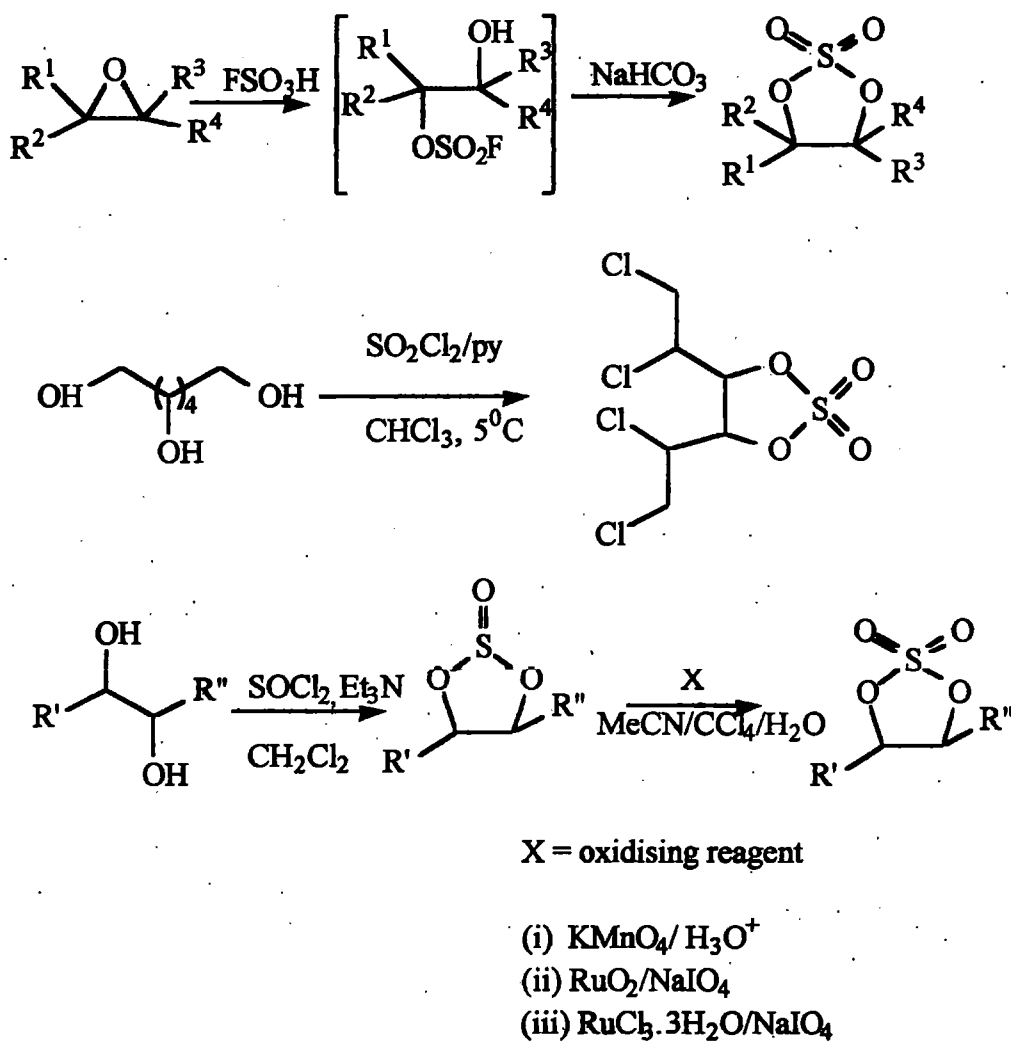
In ethylene cyclic sulfate, all the protons are magnetically equivalent⁸⁷. It has a ring strain-energy⁸⁸ of ~ 5 - 6 kcal/mol. The dipole moment of the cyclic sulfate ($\mu = 5.64$ D in dioxane) and of the tetramethyl cyclic sulfate ($\mu = 6.05$ D in dioxane) suggests that the ring is nonplanar⁸⁹

The high reactivity of cyclic sulfates has been attributed to ring-strain and the good leaving group ability of the ROSO_3^- moiety. Even though the origin of the ring-strain is not very clear, it has been speculated that, it might be due to:

- (i) angle strain, (ii) partial double bond character between the ring oxygens and the sulphur atom, as a result of a $2p(\text{O})$ - $3d(\text{S})$ orbital interaction and (iii) 1,3-nonbonding interactions between the ring oxygen and the exocyclic oxygen.

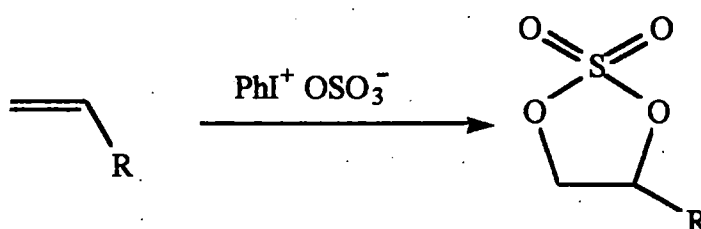
3.8.2. The synthesis of cyclic sulfates

1, 2-cyclic sulfates synthesised from diols via cyclic sulfites have been reported by Sharpless and his group⁹⁰. Several methods exist for the synthesis of this important class of organic compound⁹¹, most of which involves the oxidation of cyclic sulfites⁹². Some of these preparative methods are summarized in Scheme 3.50



Scheme 3.50

In our Laboratory, after several failed attempts to prepare silyl cyclic sulfates from the traditional one pot synthesis methods shown in the above Scheme, Xu⁹³ modified the method was able to isolate pure silyl cyclic sulfates in a two-step synthesis in 70% yield. Ethylene cyclic sulfate and the 4-butyl derivative have been prepared in 70- 85% yield by the reaction of the corresponding olefin with an hypervalent organoiodine complex, phenyliodosulfate (PhIOSO₂O)(Scheme 3.51)⁹⁴.



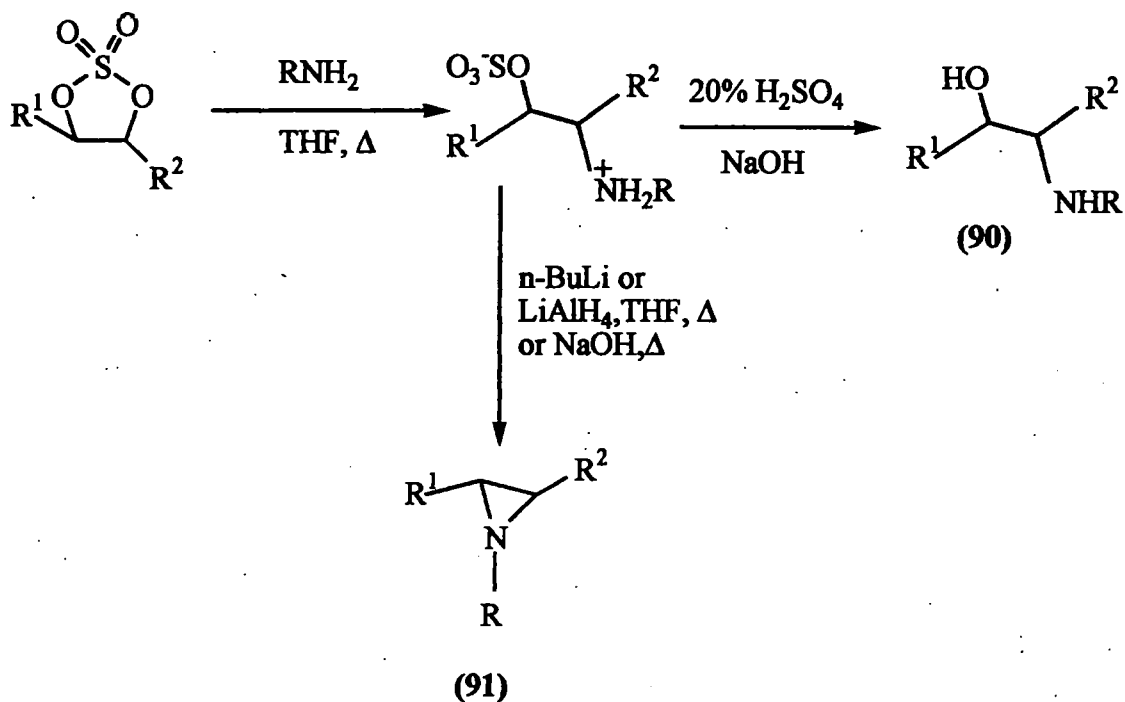
Scheme 3.51

This direct transformation of olefins to the cyclic sulphates (scheme 3.51) seemed to provide a very attractive route to silylaziridines and epoxides. However the traditional way of preparing the complex by the reaction of sulphur trioxide (SO₃) with iodosobenzene is very severe and not suitable for preparation of the silyl derivatives. We thus undertook an exploration of the synthesis of this efficient reagent and its subsequent reactions with olefins.

3.8.3 The synthesis of aziridines

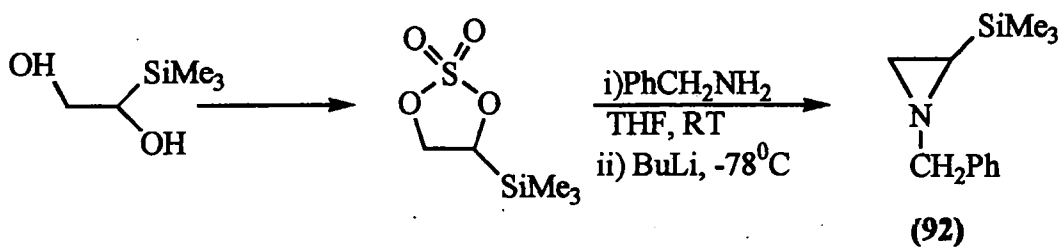
Cyclic sulfates have been shown to react readily with a wide variety of nucleophiles with apparent complete selectivity⁹⁵ to give aziridines and amino alcohols. In all ring openings of the sulfates, the first formed product is the β-sulfate, which can be hydrolysed to the β-hydroxy compound 90⁹⁶. It is in this sense that cyclic sulfates are synthetically equivalent to epoxides, however unlike the β-hydroxyl group generated in epoxide openings, the

corresponding β -sulfate moiety is itself a good leaving group. Primary amines were found to react with cyclic sulfates to give β -aminosulfates, which can be converted to the corresponding aziridine by treatment with base (Scheme 3.52).



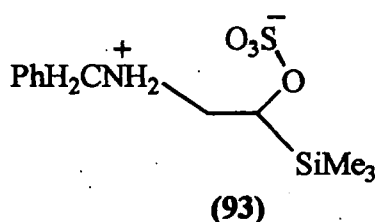
Scheme 3.52

Xu, prepared 2-trialkylsilyl aziridines using a modified Sharpless procedure via silylated cyclic sulfates⁹⁷. The reaction of the primary amine and the silylated cyclic sulfate was carried out at room temperature, in THF. After 24hrs of stirring, the reaction mixture was cooled to -78°C and then reacted with $n\text{-BuLi}$ (Scheme 3.53).

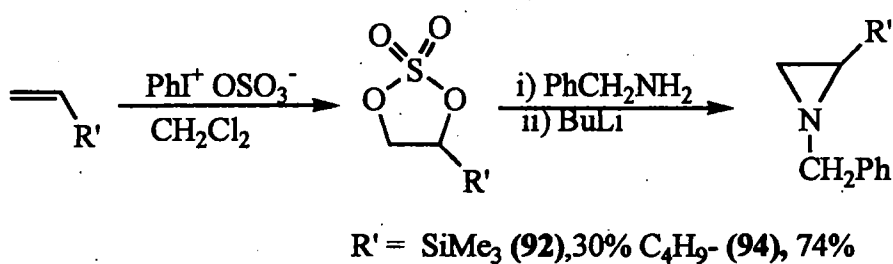


Scheme 3.53

The nucleophile, benzylamine attacks the cyclic sulfate at the β -carbon to form the α -aminosulfate **93** which on addition of base cyclises to form the aziridine.



Based on this route, we have successfully repeated the synthesis of aziridines **92** and **94**⁹⁸ in 30% and 74% yield respectively (Scheme 3.54)



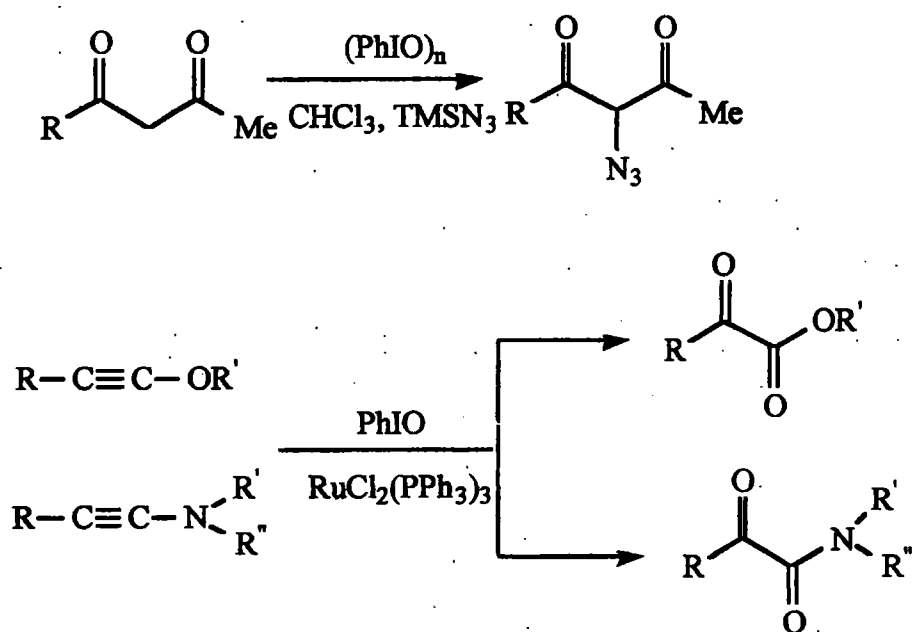
Scheme 3.54

This represents a more facile method for the synthesis of silylated aziridines via cyclic sulfates. We were unable to isolate any cyclic sulfates from functionalised vinylsilanes

and allylsilanes and hence the corresponding aziridines, could not be made by this route. Xu, also could not isolate functionalised silylated cyclic sulfates using the modified Sharpless procedure.

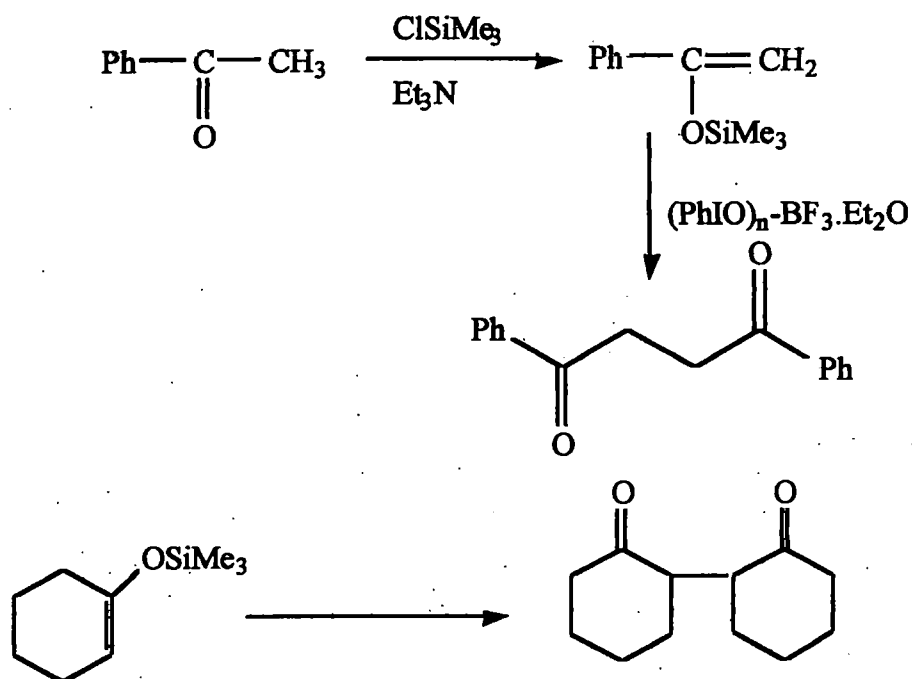
3.8.4. The Chemistry of hypervalent organoiodine complexes

In recent years there has been a considerable interest in the use of hypervalent organoiodine compounds in organic synthesis⁹⁹, most of these reactions involve oxidation¹⁰⁰. A particularly noteworthy example is the hypervalent iodine oxidation of enolisable ketones to give various α -functionalised ketones. These are useful precursors for the synthesis of a wide variety of heterocyclic compounds of medicinal interest^{101, 102}. Some typical reactions^{103, 104} are illustrated in the Scheme 3.55



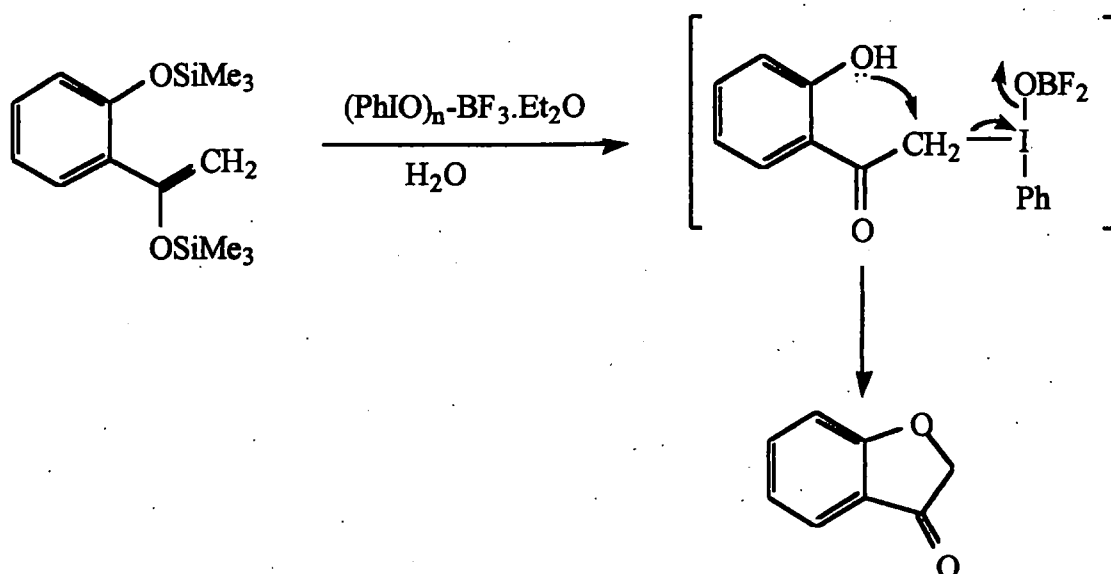
Scheme 3.55

The oxidation of silyl enol ethers with iodosobenzene and borontrifluoride diethyl etherate, has been reported to result in the formation of a carbon-carbon bond¹⁰⁵. Some examples of these carbon-carbon bond forming reactions^{106, 107} are shown in Scheme 3.56



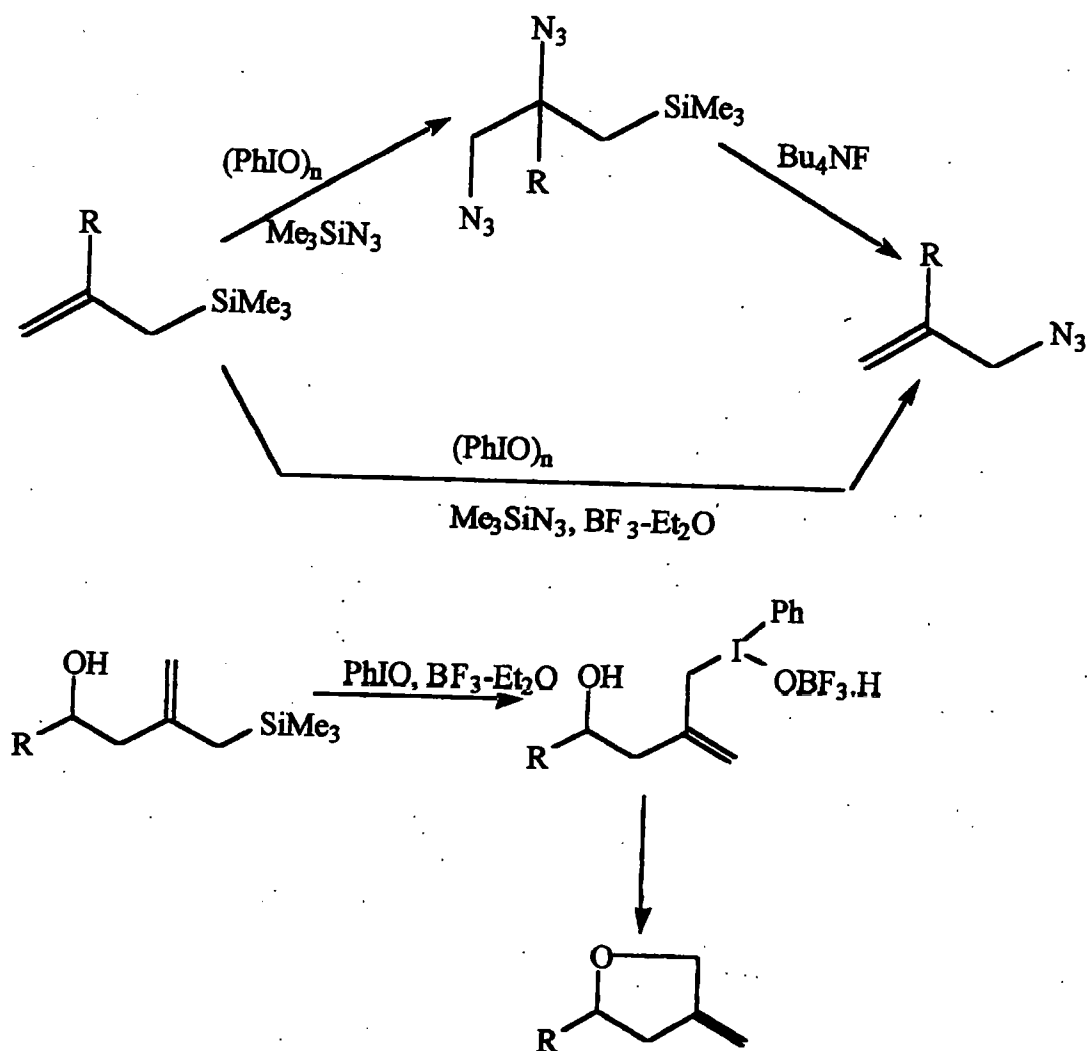
Scheme 3.56

It should be noted that the oxidation of silyl enol ethers has been used in the synthesis of coumaran-3-one, without substitution at the 2-position¹⁰⁸ (Scheme 3.57).



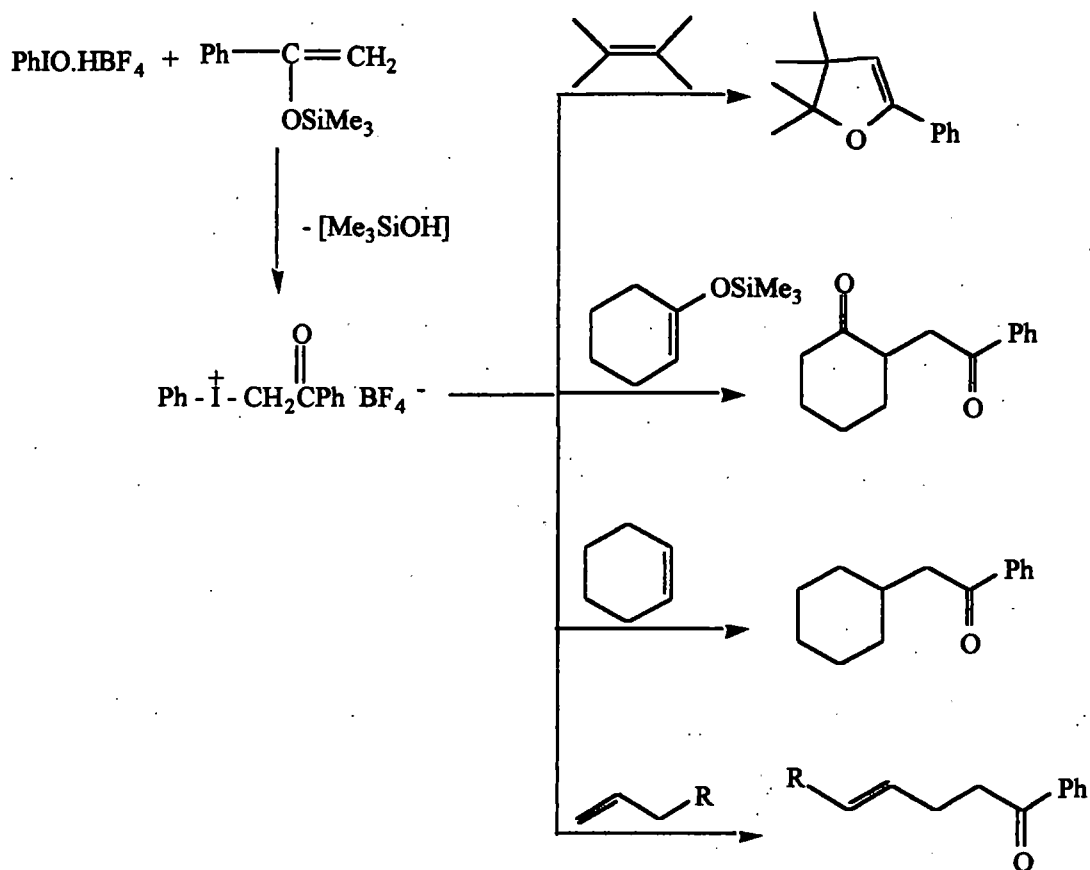
Scheme 3.57

In addition to α -functionalization of ketones, several I(III)-mediated syntheses of heterocyclic compounds have been developed, which have wide applicability. Similarly, I(III) reagents have been used in the syntheses of allylazides from allylsilanes¹⁰⁹ and also in the cyclization of allylsilanes¹¹⁰, Scheme 3.58



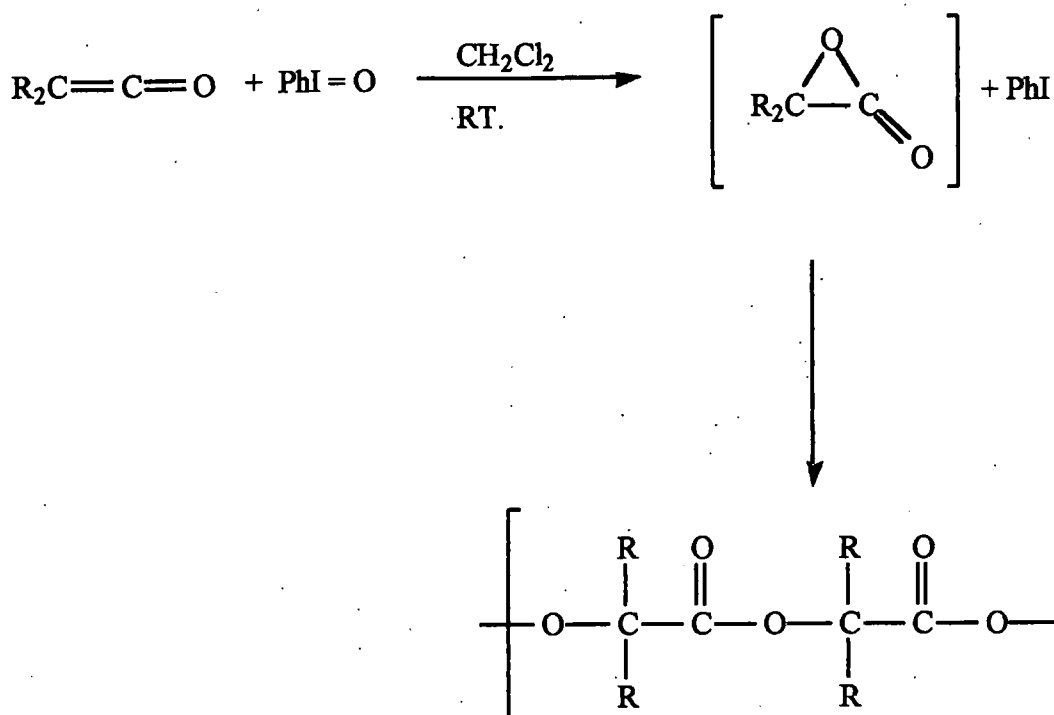
Scheme 3.58

The adduct formed between a silyl enol ether and hypervalent iodine has been shown^{111, 112} to react with alkenes to give various products each involving C-C bond formation (Scheme 3.59).



Scheme 3.59

Recently, Groves¹¹³ has shown that iodosobenzene, PhIO , could serve as a source of oxygen for a porphyrin, which in turn effected olefin epoxidation and hydroxylation. Furthermore, anaerobic oxygenation of cytochrome P450 has been achieved using PhIO , as the oxygen-atom donor^{114,115}. An example of the use of iodosobenzene as an oxygen donor is the epoxidation of ketenes to yield, initially, α -lactones which polymerize to give a polyester¹¹⁶ (Scheme 3.60).



Scheme 3.60

In an attempt to develop reagents, which would effect the transformation of olefins into synthetically valuable *vic*-derivatives, we have developed a novel reagent, based on the reaction of iodosobenzene and chlorotrimethylsilylsulfonate ester. This reagent offers a versatile means to effect a direct transformation of olefins not only into their cyclic sulfates derivatives, but also sultones. Unlike the traditional one pot synthesis of cyclic sulfates, this method was suitable for the formation of silyl derivatives.

3.8.5 The chemistry of sultones

Sultones are heterocyclic compounds containing the $-\text{O}-\text{SO}_2-$ group and are internal esters of the corresponding hydroxysulphonic acids. The term 'sultone' was introduced by Erdmann to describe one of the simplest aromatic sultones, 1,8-naphthosultone (Figure 3.2). Sultones are the sulphur analogues of lactones.

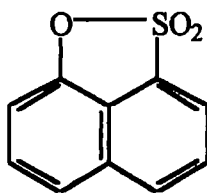


Figure 3.2

As with lactones, there exist α -, β -, γ -, δ - sultones and numerous other cyclic sulfonates. Among the unsubstituted compounds, the γ - and δ - sultones having 5- and 6-membered rings respectively, are the most stable. Unsubstituted β -sultones are known to decompose extremely readily and hence their isolation is very difficult. In contrast, fluorinated β -sultones are relatively stable¹¹⁷. Sultones, generally behave like open-chain sulfate esters and are excellent alkylating agents, reacting with bases and nucleophiles to produce the ring-opened sulfonate derivatives¹¹⁸. There is a considerable interest in the chemistry of sultones, as they have great potential as surfactants¹¹⁹, as precursors of surfactants¹²⁰ or anti-static agents¹²¹. It has been reported that derivatives of α -sulfopolyfluoro carboxylic acids prepared from β -sultones inhibit the growth of microorganisms¹²². Polyester and polyamides of α -sulfo polycarboxylic acids (Figure 3.3) are non-flammable polymeric materials¹²³.

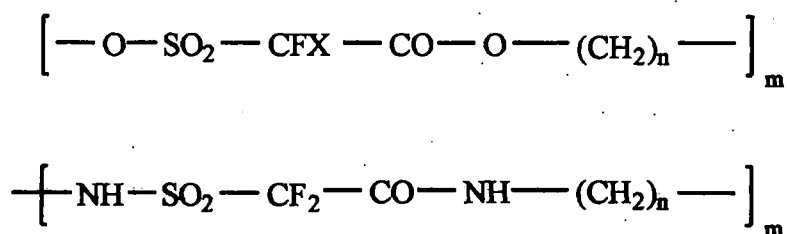
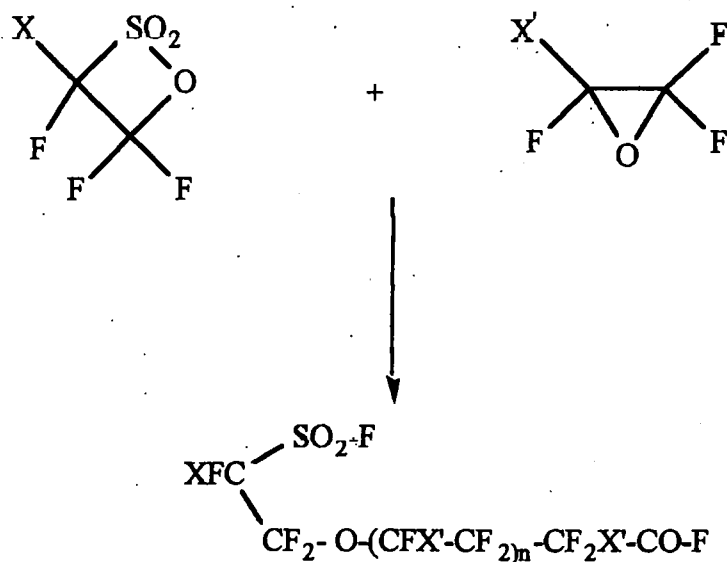


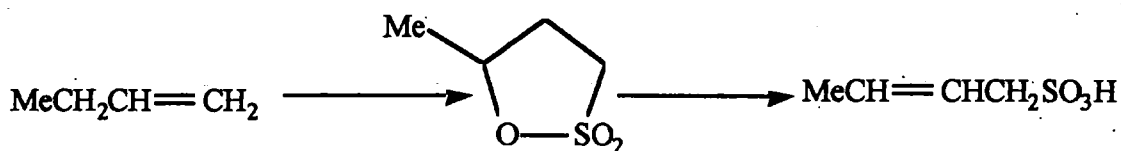
Figure 3.3

Telomerization products of β -sultones and fluorinated epoxides are also characterised by high thermal stability (Scheme 3.61)¹²⁴



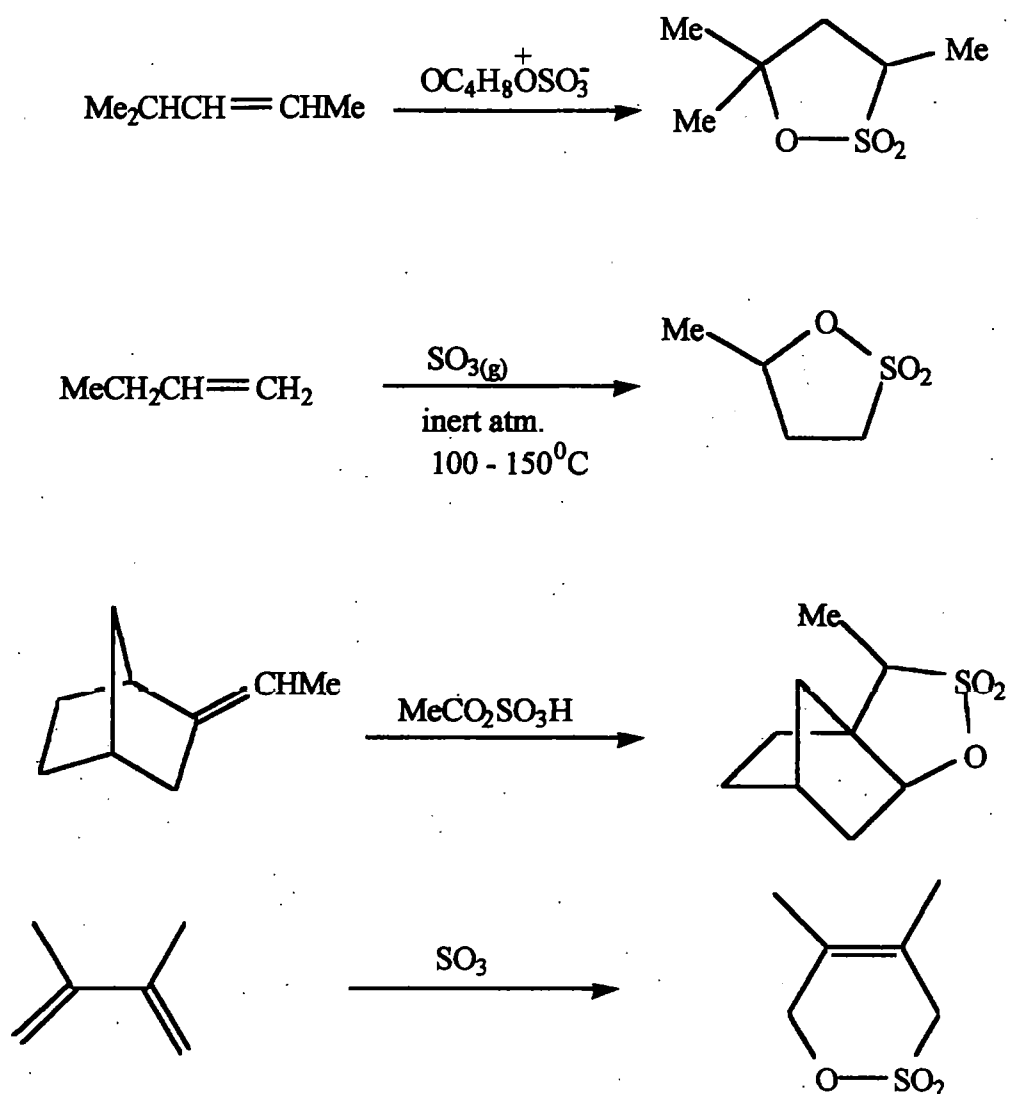
Scheme 3.61

In view of the very rich chemistry of sultones, numerous preparative methods have been devised for their synthesis. Sulphonation of alkenes is the main method of preparation. This route is used to make β - and γ -sultones in particular which can then be converted to alkenesulphonic acids (Scheme 3.62).



Scheme 3.62

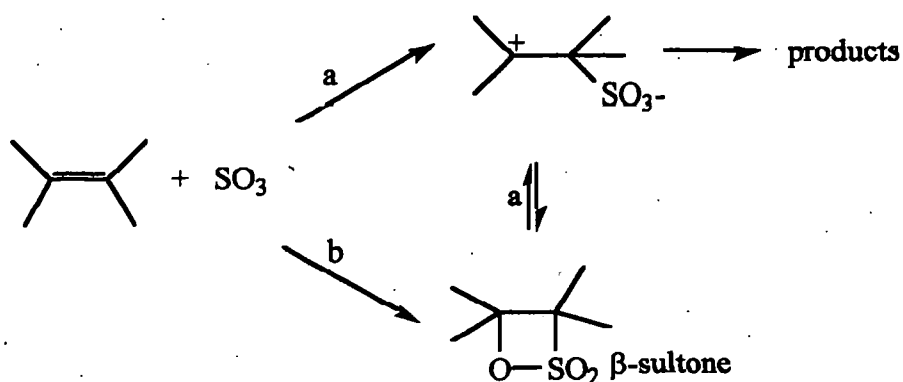
Preparation of sultones via alkene sulphonation has been extensively covered in a recent review by Roberts and Williams¹²⁵ and in earlier reviews by Breslow and Skolnik¹²⁶ and Mustafa¹²⁷. Addition of sulphur trioxide to unsubstituted olefins proceeds extremely readily and is so exothermic that the primary adduct is very difficult to trap. It is therefore necessary to subdue the electron-acceptor properties of the sulphur trioxide. This is readily accomplished by forming adducts of the sulphur trioxide. A variety of sulfonation reagents have been used in the preparation of sultones, these include Lewis-base complexed sulphur trioxide such as SO₃-dioxane¹²⁸, introduced by Suter¹²⁹ in 1938, SO₃-pyridine¹³⁰, SO₃-triethylamine¹³¹ and gaseous SO₃¹³². Most recently acetyl sulphate has been used in the sulphonation of ethylenenorbornane to produce the γ -sultone¹³³. Some of these preparations are summarised in Scheme 3.63



Scheme 3.63

There is evidence from spectroscopic studies¹³⁴ and trapping experiments¹³⁵ that the sulphonation of alkenes using SO_3 leads initially to β -sultones. However, under the reaction conditions, these β -sultones are unstable short-lived species which rearrange to give larger rings. For the formation of β -sultones, two possible mechanisms may be considered. For simple alkenes and fluoro-olefins¹³⁶, it is generally assumed that the first step is electrophilic attack of sulphur trioxide on the double bond. In agreement with

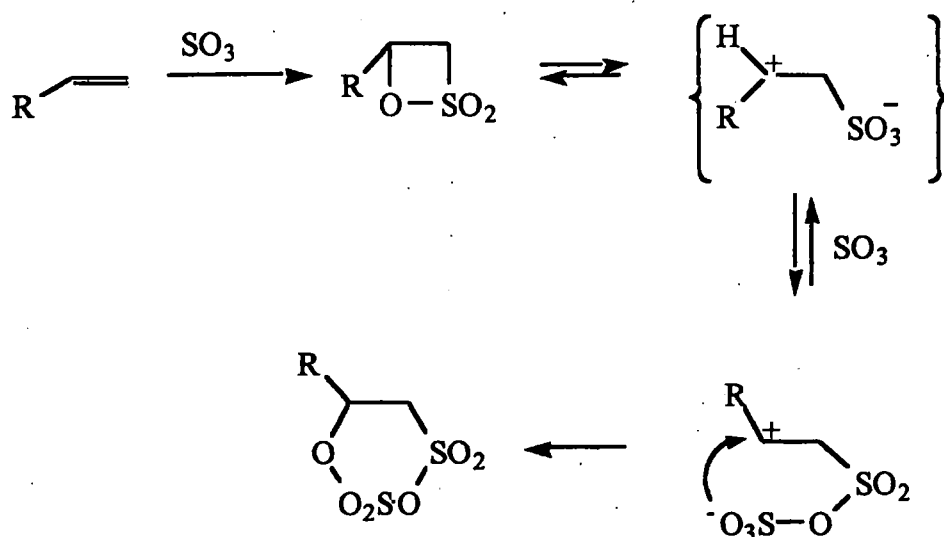
Markovnikov's rule, a zwitterionic intermediate¹³⁷ is formed which undergoes reversible cyclization to form the β -sultone (path a), Scheme 3.64.



Scheme 3.64

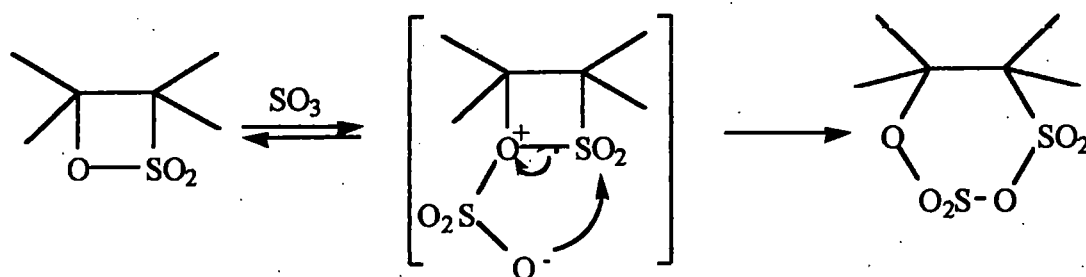
As an alternative mechanism (path b), the β -sultone is formed directly via a concerted thermal cycloaddition¹³⁸.

The sulfonation of alkenes with an excess of sulfur trioxide has been reported to lead to a sulfonate-sulfate anhydride (carbyl sulfate)¹³⁹. Bordwell¹⁴⁰, was able to show that the sulfonation of 1-hexene with a 2 mol-equivalent of SO_3 complexed with dioxane is a two step process. The rapid formation of β -sultone is followed by a slow uptake of a second mole of SO_3 to give the carbyl sulfate (Scheme 3.65).



Scheme 3.65

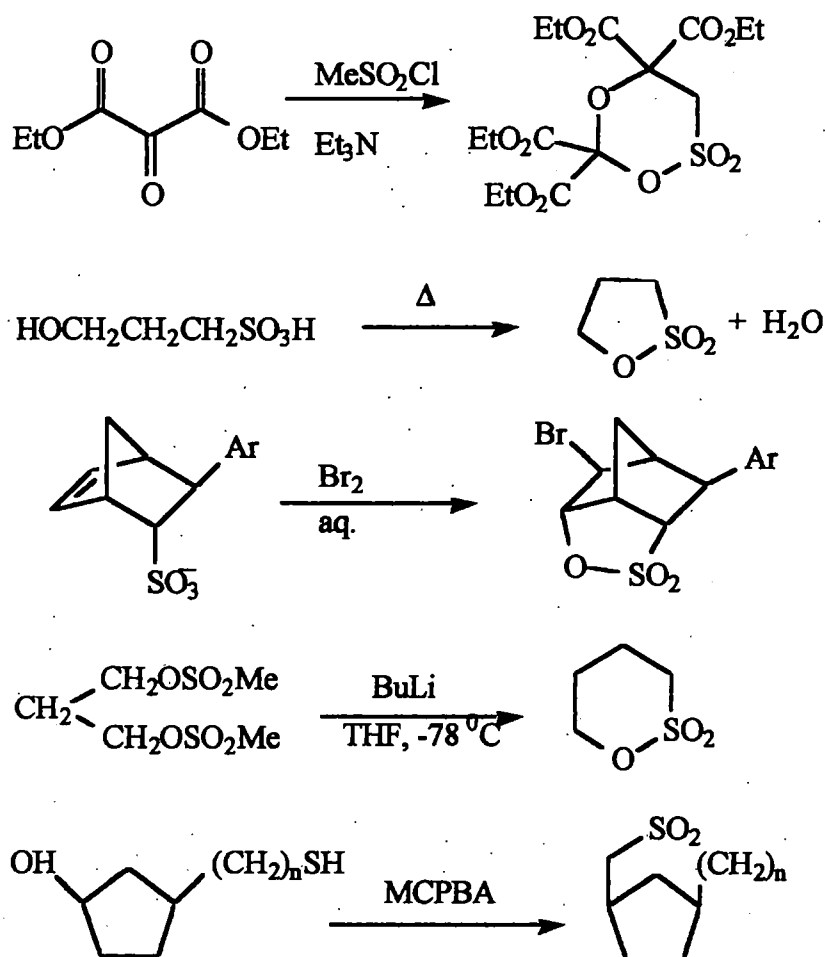
The formation of the β -sultone and the insertion of the SO_3 into the β -sultone to give the carbyl sulfate proceeds stereospecifically. A possible mechanism for the stereospecific formation of carbyl sulfate is depicted in Scheme 3.66. The insertion of SO_3 probably occurs into the $\text{O}-\text{SO}_2$ bond.



Scheme 3.66

Methods of preparation of sultones include the reaction of sulphenes with carbonyl compounds¹⁴¹ and thermal cyclization of halogeno or hydroxyalkanesulphonic acids¹⁴². Similarly, reactions of alkenesulphonate salts with dihalogens, (halosultonation)¹⁴³ and

metallation of alkanesulphonate esters of alcohols, which have been functionalised at the 2- or 3- positions, lead to γ - and δ - sultones¹⁴⁴. Other preparations of sultones include the oxidation of sulphur compounds¹⁴⁵ and the insertion of SO_3 into various bonds¹⁴⁶. A summary of these routes is depicted in Scheme 3.67.



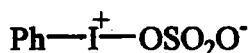
Scheme 3.67

Addition of sulphur trioxide to olefins proceeds extremely readily and is so exothermic that the primary adduct is very difficult to trap and always results in a series of complicated reaction and by products. In view of this, we developed a new method of producing a sulphur-trioxide adduct under mild conditions without the use of the extremely dangerous sulphur trioxide gas. Its subsequent one pot reaction with olefins has reproducible results and fewer by-products.

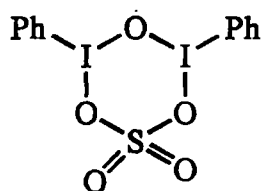
This section describes the generation of phenyliodosulfate ($\text{PhI}^+\text{OSO}_3^-$) from the reaction of iodosobenzene and chlorotrimethylsilyl sulfonate ester ($\text{ClSO}_2\text{OSiMe}_3$) in dichloromethane and its subsequent reaction with olefins, under different conditions to give either the corresponding cyclic sulfates or sultones.

3.8.6.1. Phenyliodosulfate.

This reagent can be considered to be a 1,4 -dipole and is obtained by the interaction of PhIO (iodosobenzene) with either one equivalent or half an equivalent of chlorotrimethylsilyl sulfonate ester ($\text{ClSO}_2\text{OSiMe}_3$) at -78°C in dry dichloromethane giving the sulfates **95** and **96** respectively.

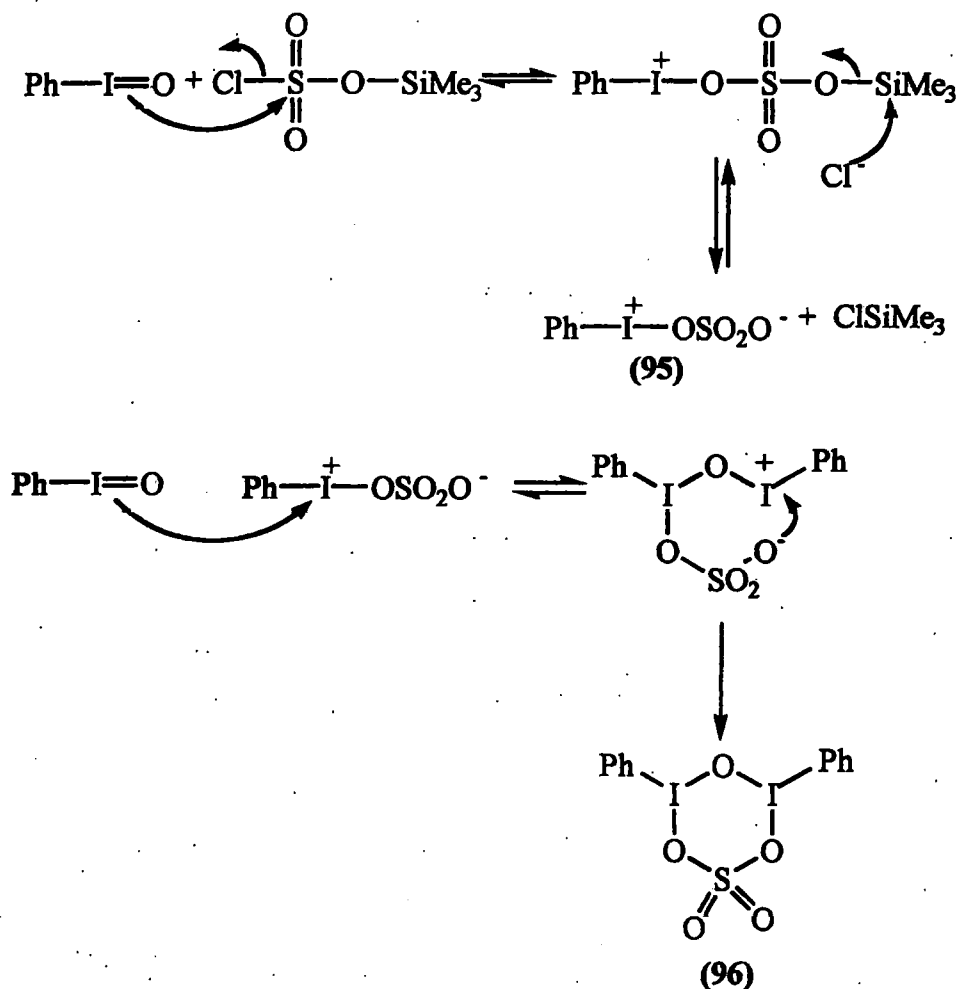


(95)



(96)

These were isolated as very moisture sensitive powders. The preferred mechanism for the formation of these highly reactive iodonium salts is depicted in Scheme 3.68.

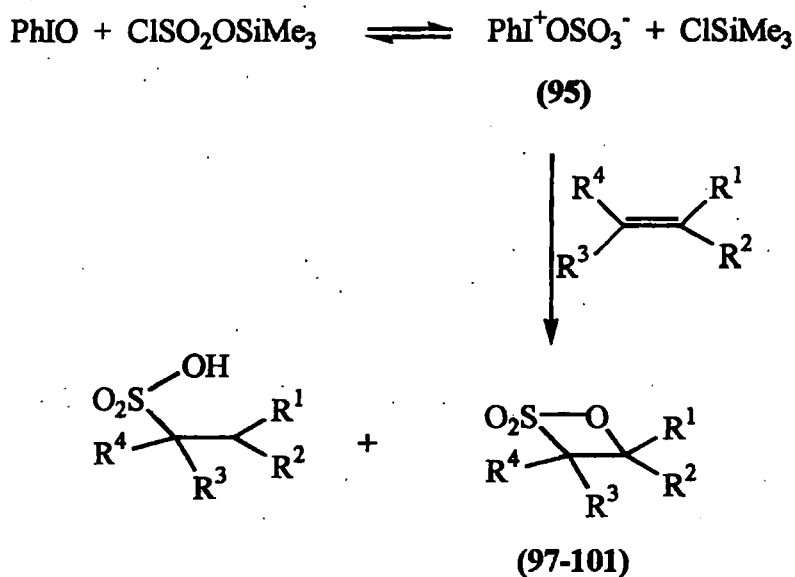


Scheme 3.68

Because of the reactive nature of these species, they were generated *in situ* before reaction with alkenes.

3.8.6.2. Synthesis of sultones

We have found that iodosylbenzene reacts with $\text{ClSO}_2\text{OSiMe}_3$ (1 equivalent) in dry dichloromethane under an inert atmosphere at -78°C to produce a yellow solution of **95**, stable up to 0°C and decomposing to give a black tar only at high temperatures. Addition of alkenes (1 equivalent), to this yellow solution, (in the presence of the ClSiMe_3 that is produced) at -78°C led to immediate reaction, to give a colourless solution. This was allowed to warm up to room temperature and then worked up by removing any excess reactant or solvent using a rotatory evaporator. This gave a dark residue, which was purified by column chromatography with silica gel using hexane/ CH_2Cl_2 as the eluent. In all cases, sultones were produced together with sulfonic acids. This is shown in Scheme 3.69



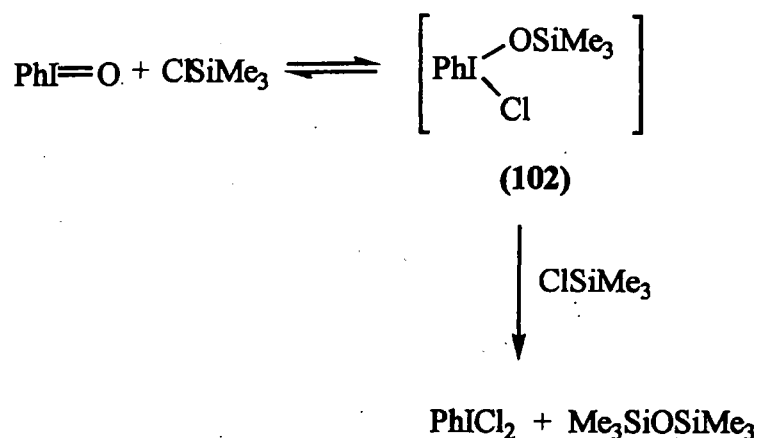
Scheme 3.69

The sultones formed are summarised in Table 3.1

Table 3.1 β -sultones obtained from various alkenes

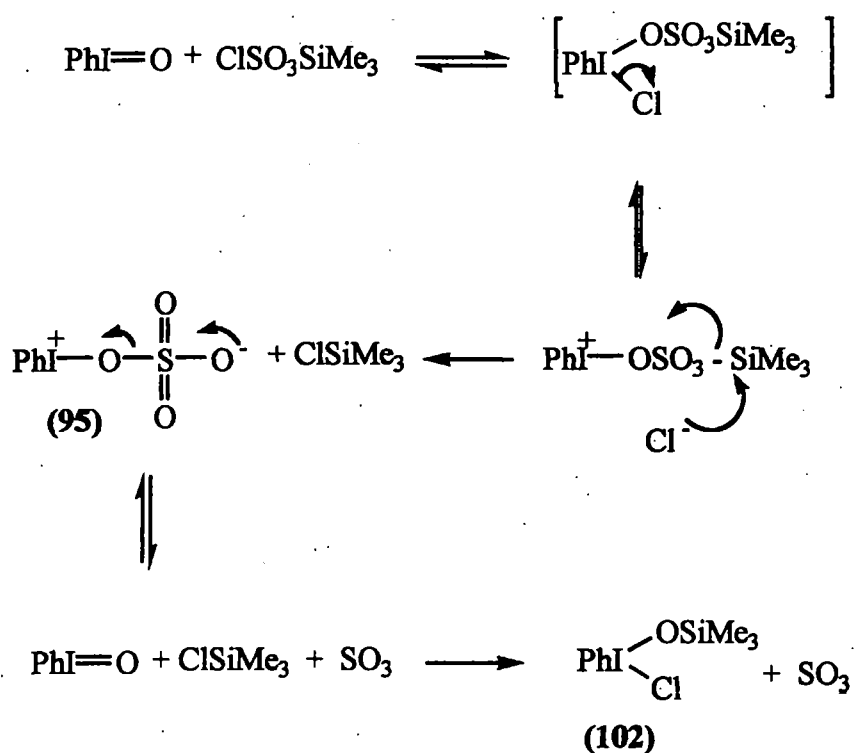
Entry	β -sultone				% yield
	R ¹	R ²	R ³	R ⁴	
97	H	SiMe ₃	H	H	57
98	H	C ₄ H ₉	H	C ₄ H ₉	65
99	H	C ₄ H ₉	C ₄ H ₉	H	50
100	Ph	H	Ph	H	60
101	Ph	H	H	Ph	55

The sulfonating complex **95** (still in the presence of the ClSiMe₃ produced) is a good source of SO₃, which adds to the alkenes to form mainly the β -sultone. Other products identified were hydroxy sulfonic acids and alkene sulphonic acids. In order to explain the generation of the sultone and not the expected cyclic sulphate, we reacted PhIO and ClSiMe₃ in molar ratios of 1:1 and 1.5:1 in deuterated acetonitrile. The reactions were performed at -78°C and at room temperature in each case. All experiments resulted in the formation of hexamethyldisiloxane and a yellow solid, which was confirmed to be iodosobenzene dichloride (PhICl₂), by independent synthesis¹⁴⁷. A possible mechanism for this reaction involves the nucleophilic attack of the iodosobenzene on chlorotrimethyl silane to generate the tricoordinate iodine species **102**. This is more reactive than the PhIO, hence reacts further with ClSiMe₃ to give the disiloxane (Scheme 3.70)



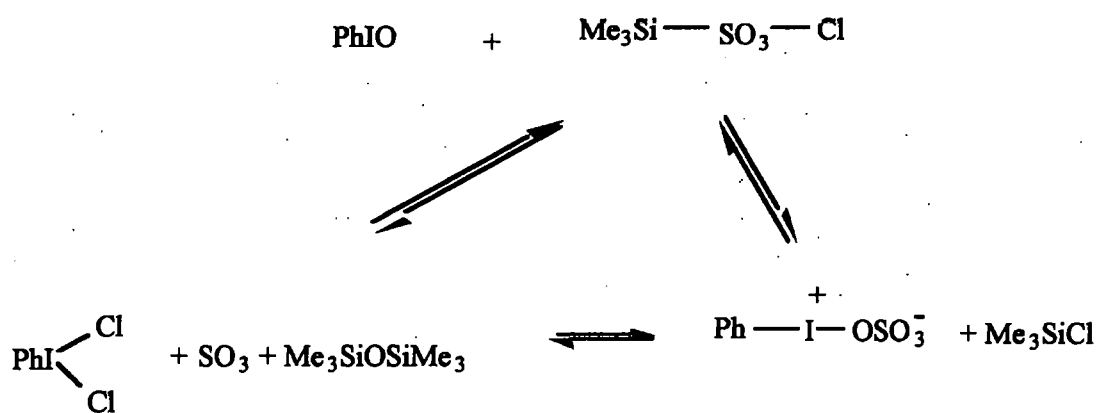
Scheme 3.70

By analogy, we may expect that the reaction of iodosobenzene with chlorotrimethylsulfonate ester first form a tricoordinate species, which then collapses to form **95**, as shown in scheme 3.71. The liberated ClSiMe_3 will then react with the iodosobenzene as discussed in scheme 3.70, leading to free SO_3 . This then reacts with the added olefins in the usual manner, to give the sultones.



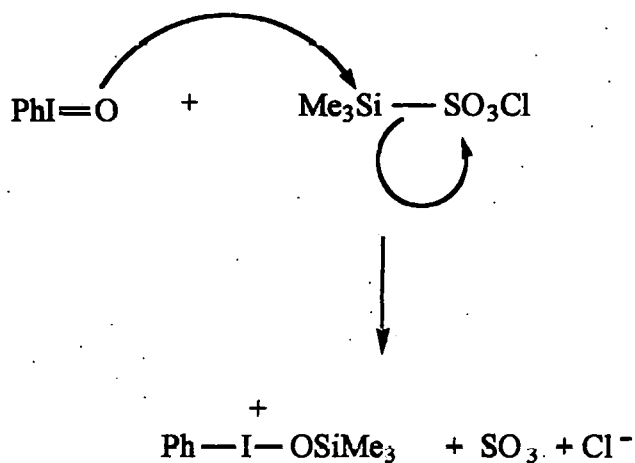
Scheme 3.71

The above mechanism can also be better treated as a competing equilibrium, Scheme 3.72.



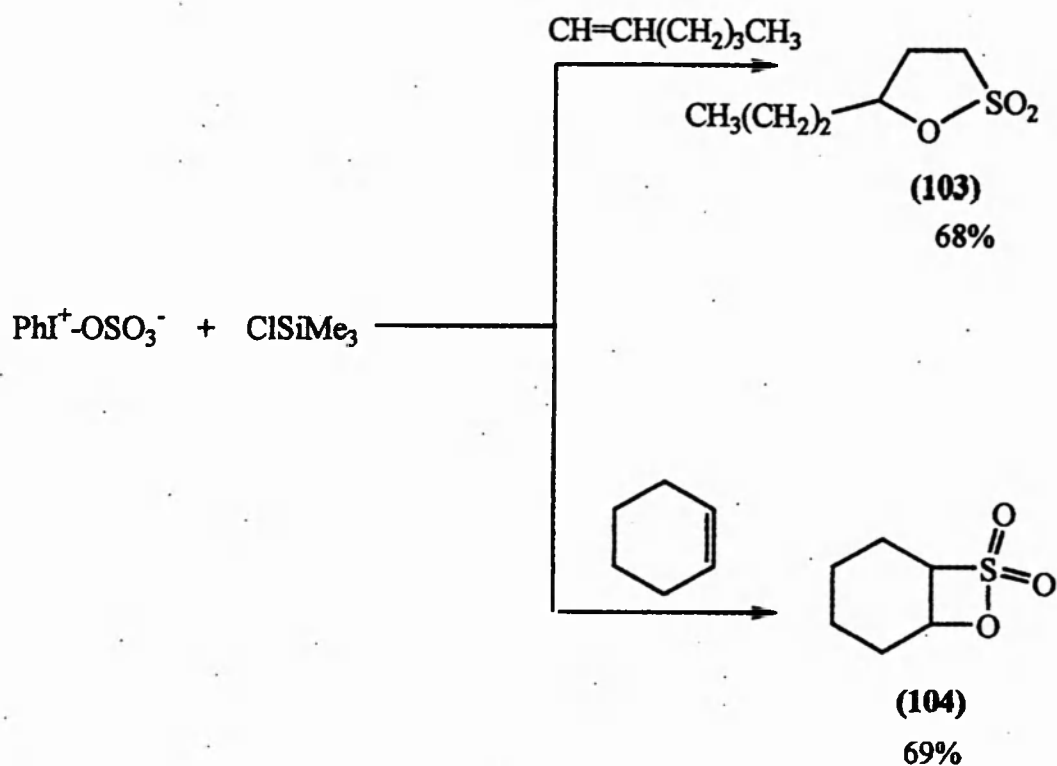
Scheme 3.72

It is possible that the mechanism could involve a direct reaction of the iodosobenzene with the chlorotrimethylsilyl sulphonate ester to liberate SO_3 , which then adds to our alkene, Scheme 3.73.



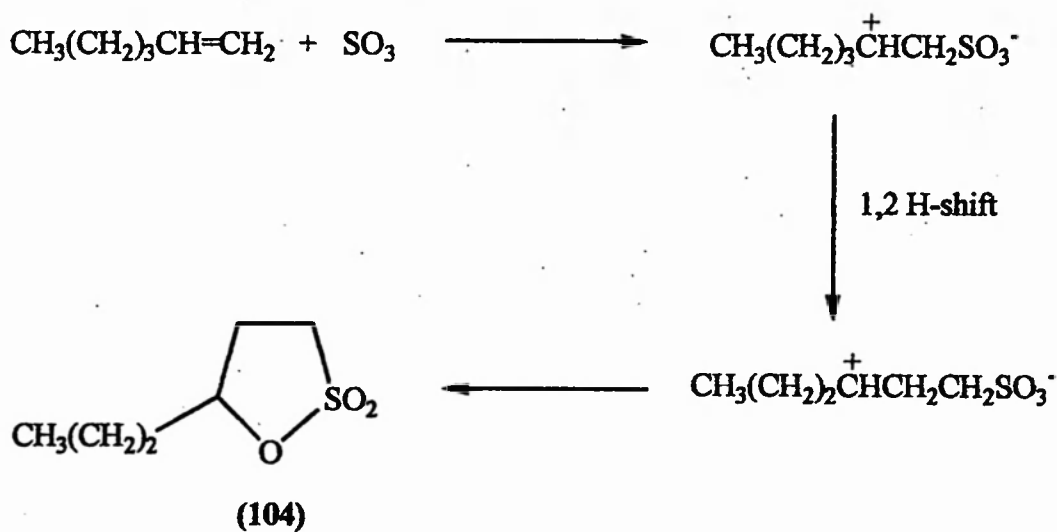
Scheme 3.73

The addition of a linear terminal alkene such as 1-hexene, was found to give the γ -sultone **103** together with the corresponding alkene sulphonic acid. However with cyclohexene, the β sultone **104** was isolated, Scheme 3.74.



Scheme 3.74

The formation of γ - sultones, such as **104**, has been rationalised in terms of a hydride shift during sulfonation¹⁴⁸ as depicted in the mechanism Scheme 3.75.



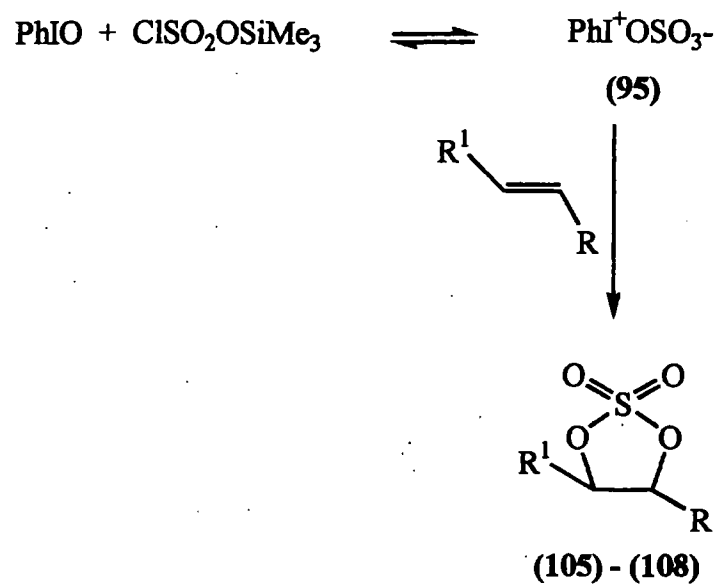
Scheme 3.75

Although the sulfonation of olefins with SO_3 has been extensively investigated, the stereochemical outcome of the reactions has not been widely studied. It has been reported however, that the sulfonation of *cis*- and *trans*-but-2-ene with a SO_3 -dioxane complex proceeds stereospecifically yielding *cis*- and *trans*-2,3-butanedisulfone respectively¹⁴⁹. The reaction of our reagent with *cis*- and *trans*-5-decene and *cis*- and *trans*-stilbene was also very stereospecific yielding the corresponding disulfone.

3.8.6.3. Synthesis of cyclic sulfates via iodonium ylids

It has already been shown that the addition of alkenes, to the iodonium ylids **95** or **96**, resulted in the formation of the corresponding cyclic sulfate⁹⁴.

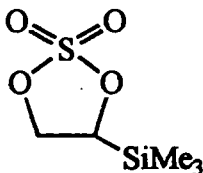
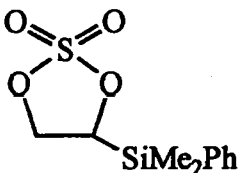
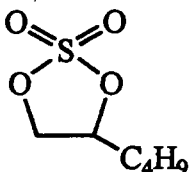
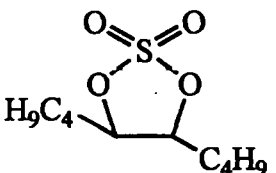
In our one pot method for the synthesis of cyclic sulfates, we have found that iodosylbenzene reacts with $\text{ClSO}_2\text{OSiMe}_3$ (1 equivalent) in dry dichloromethane under an inert atmosphere at -78°C to produce a yellow solution of **95**. Removal of the ClSiMe_3 produced followed by addition of the alkene (1 equivalent), to this yellow solution, at -78°C led to an immediate reaction, to give a colourless solution. The reaction mixture was allowed to warm up to room temperature and then worked up, by removing any excess reactant or solvent using a rotatory evaporator. This gave a dark residue, which was purified by column chromatography over silica gel using hexane/ CH_2Cl_2 as the eluent. In all cases, cyclic sulfates were obtained as shown in Scheme 3.76.



Scheme 3.76

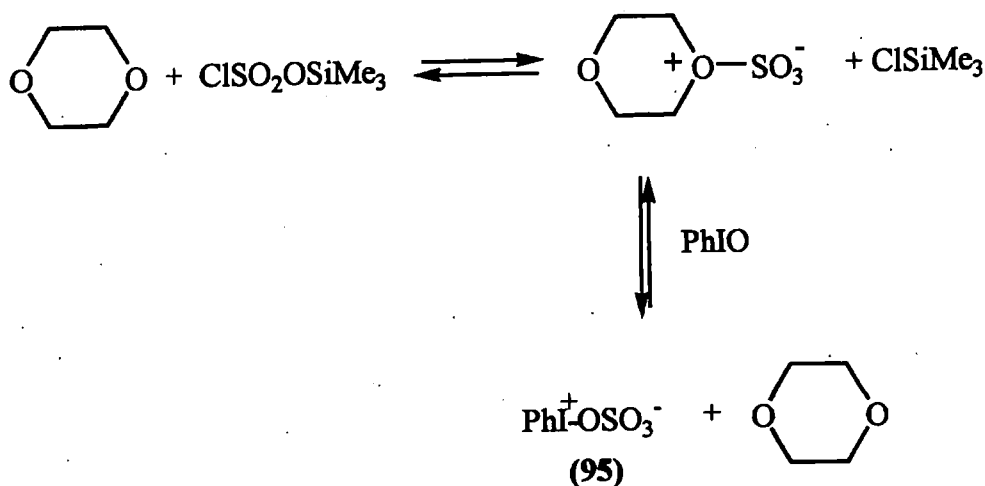
Table 3.2

Summary of the cyclic sulphates formed.

	Cyclic sulphate	Yield (%)
105		76
106		65
107		66
108		50

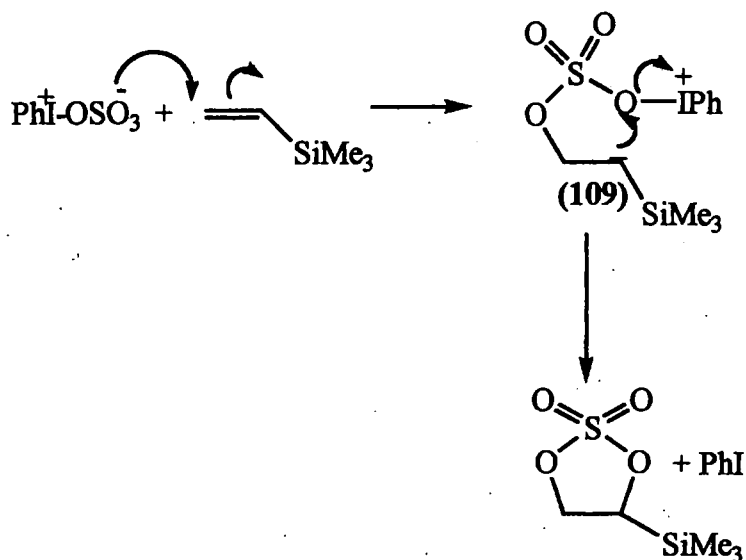
It is interesting to note that the presence or absence of ClSiMe_3 in the reaction system seems to determine whether a sultone or cyclic sulfate will be formed. In this preparation, removal of the chlorotrimethylsilane prevents the formation of the sulphur trioxide and hence the corresponding sultone. To investigate further the influence of chlorotrimethylsilane on the outcome of the reaction, $\text{ClSO}_3\text{SiMe}_3$ was first reacted with dioxane¹⁵⁰ and then the ClSiMe_3 produced was distilled off. PhIO was then added to the resulting adduct, at -78°C in dry dichloromethane to

give a yellow complex, Scheme 3.77, believed to be **95**. After stirring at this temperature for about 10mins, vinyltrimethylsilane was added and the mixture allowed to warm up to room temperature. The reaction was worked up as before and was found to give cyclic sulfate **105**. Repeating this modified method with 1-hexene also resulted in the formation of **107**.



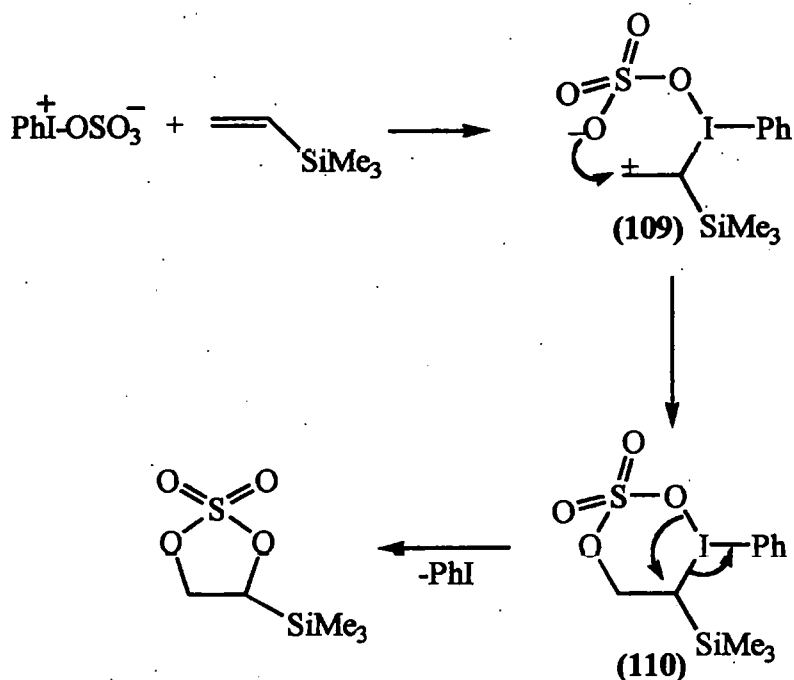
Scheme 3.77

The mechanism of formation of cyclic sulfates, from the reaction of vinyltrimethylsilanes with species **95**, can be thought of as a nucleophilic attack on the alkene double bond to give the intermediate **109** followed by cyclization resulting in the loss of iodobenzene and formation of the cyclic sulfate (Scheme 3.78).



Scheme 3.78

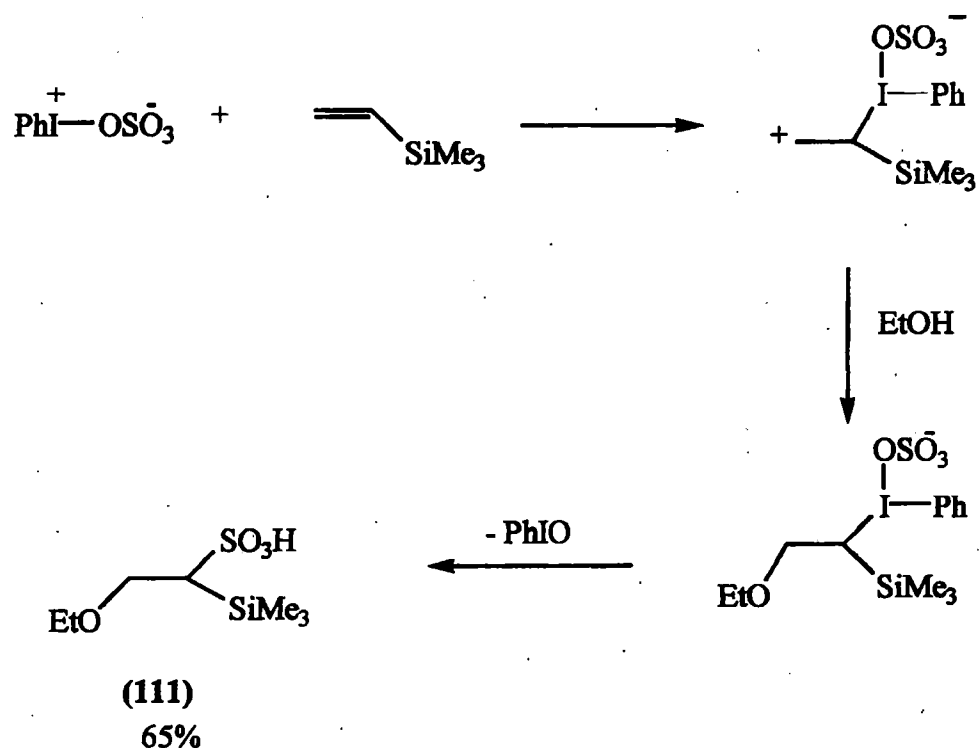
An alternative explanation for the formation of these cyclic sulfates involves a carbocationic mechanism. First electrophilic attack of the iodine atom on the alkene double bond gives the intermediate 109, which will then cyclise to 110. Reductive elimination of iodobenzene, results in the formation of the cyclic sulfates (Scheme 3.79).



Scheme 3.79

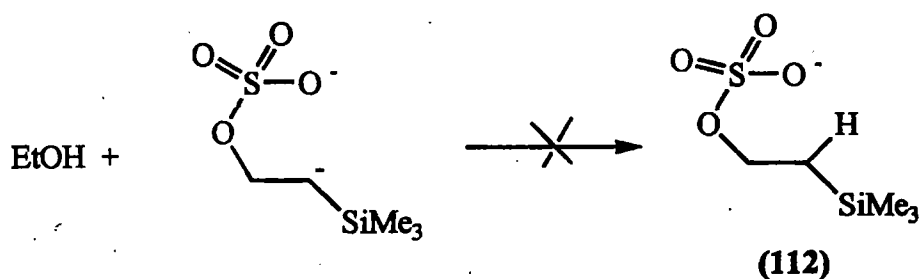
To differentiate between the mechanisms, we performed a trapping experiment by generating **95** in the presence of trace amounts of ethanol in dichloromethane.

Surprisingly, an ethoxysulfonic acid was produced, Scheme 3.80.



Scheme 3.80

This rules out the mechanism shown in Scheme 3.78. If the reaction proceeded through such a mechanism the trapping experiment will have produced **112** which was not observed,



For further confirmation of this mechanism, the cyclic sulfates were prepared in an ethanol-free system. The isolated sulfates were then treated with ethanol in dichloromethane, but no reaction was observed.

3.9 Chapter Three References

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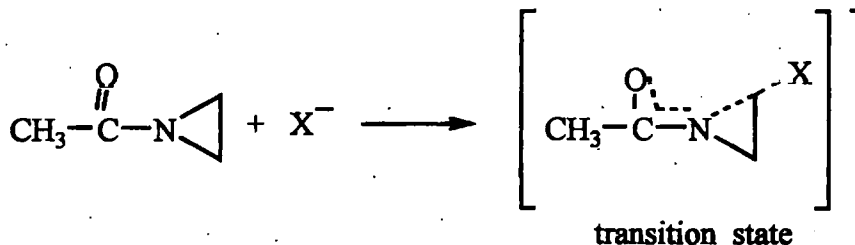
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Ring-opening reactions of β -trialkylsilylaziridines

4.1 Introduction

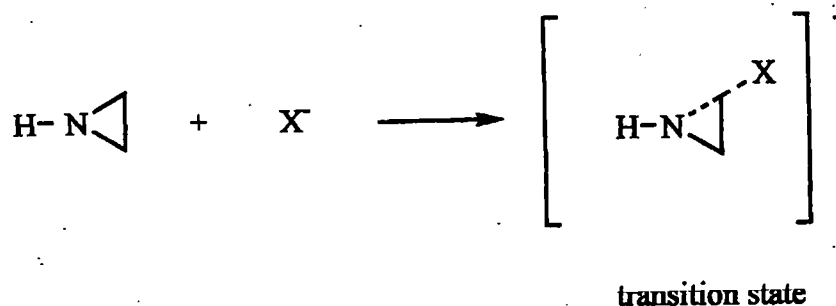
The ring-opening reactions of three-membered heterocyclic compounds is favoured by the ring strain. Thus, ring-opening reaction may be formulated as nucleophilic substitutions involving attack of a nucleophile at an aziridine carbon. Aziridines can be broadly divided into two groups of compounds based on their reactivity towards nucleophilic reagents; activated aziridines and non-activated (basic) aziridines¹.

Activated aziridines are those which contain substituents capable of stabilising the negative charge which is formed on the aziridine nitrogen in the transition state when the compound reacts with a nucleophile, as shown in Scheme 4.1.



Scheme 4.1

Basic aziridine do not have such stabilising substituents and the negative charge becomes localised on the nitrogen, Scheme 4.2.

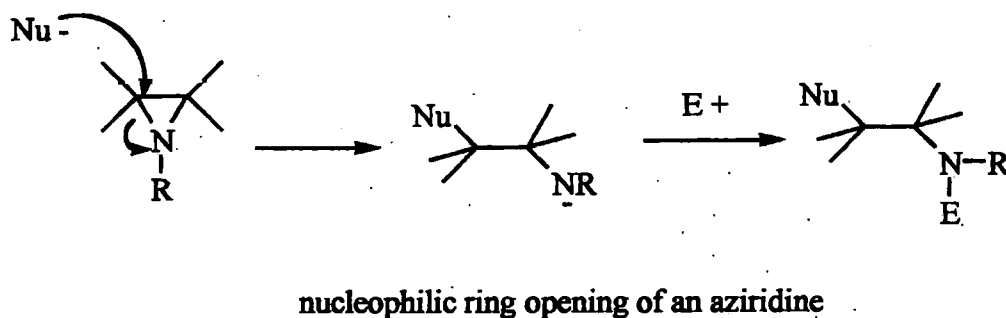


Scheme 4.2

The ability of substituents to conjugate with the partial negative charge on the aziridine nitrogen greatly reduces the activation energy needed to attain the transition state². Such compound will readily undergo ring-opening reaction with nucleophilic reagents such as amines even in the absence of acid catalysts³.

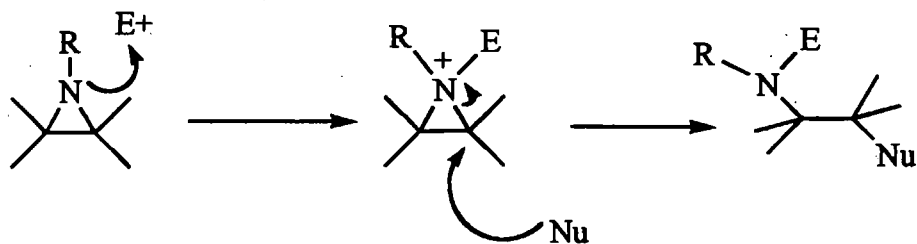
4.2 Ring opening reactions of non-silylaziridines

Ring opening reactions may occur by direct nucleophilic attack as shown in Scheme 4.3,



Scheme 4.3

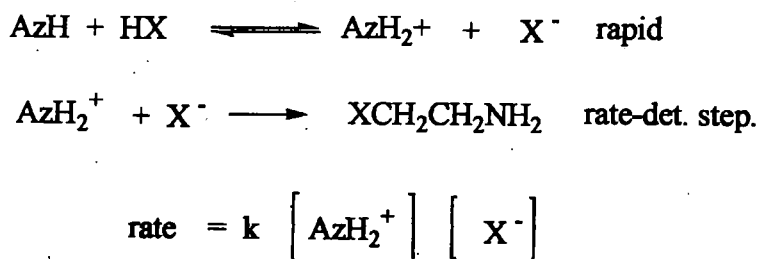
or by the electrophilic attack of the reagent with nitrogen to form an intermediate aziridinium salt which is subsequently attacked by the corresponding anion, Scheme 4.4.



electrophilic ring opening of an aziridine

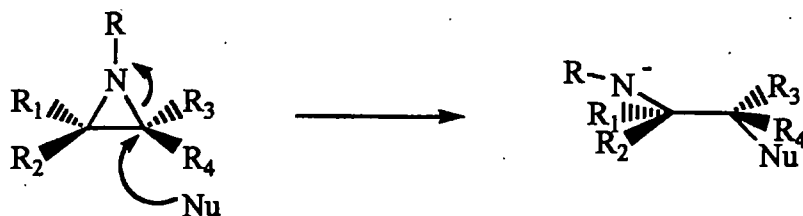
Scheme 4.4

Electrophilic ring-opening of aziridines usually depends on the reactivity of the protonated or quaternized aziridine. The kinetic expression for ring opening of a basic aziridine (AzH) with a halogen acid (HX) is given in Scheme 4.5⁴.



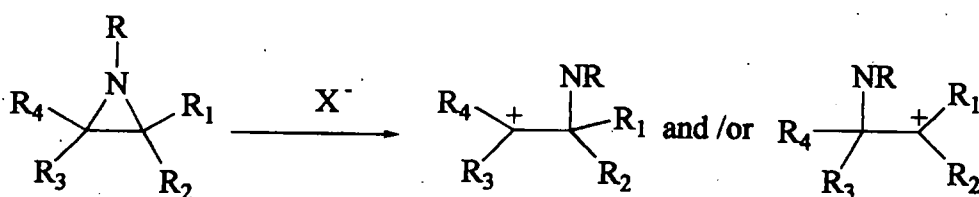
Scheme 4.5

In all cases, attack occurs with the substrate undergoing a Walden inversion⁵; the nucleophile attacking the carbon at the opposite side to the heteroatom. This Walden inversion, suggests an " $\text{S}_\text{N}2$ "-type mechanism as shown in Scheme 4.6.



Scheme 4.6

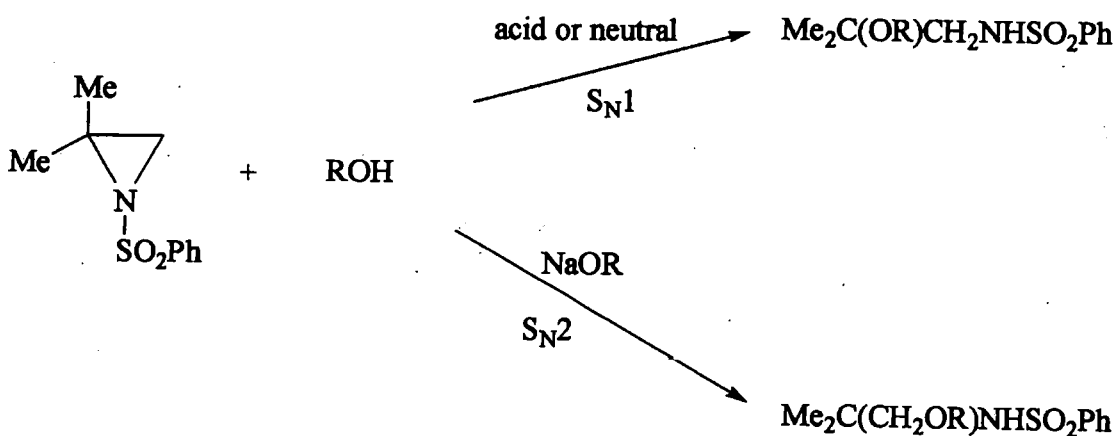
“ S_N2 ”-type mechanisms predominate with aziridines which have primary carbons i.e. where $R_1=R_2=H$ and/or $R_3=R_4=H$. However, for aziridines with substituents on the ring carbons, the mechanism for the ring opening reaction is not clearly defined and can be either S_N1 or S_N2 ¹. It has been suggested that the latter process dominates with aziridines with secondary carbon atoms and the former is the main path for aziridines with tertiary carbon atoms⁶. However, an accurate representation of the ring-opening process cannot be adequately described using the classical S_N1 and S_N2 mechanisms. In general, the presence of alkyl groups at one of the aziridine carbons increases the rate of ring-opening by nucleophiles⁶. Alkyl groups on the aziridine nitrogen cause a decrease in rate compared to that for the unsubstituted compound. However, if the alkyl group on the nitrogen contains an electronegative group such as OAc, or CN, the rate is increased. When an unsymmetrically carbon-substituted aziridine undergoes ring-opening via an S_N1 process, formation of two carbocations are possible, leading to two isomers (Scheme 4.7).



Scheme 4.7

It would appear that unsymmetrically carbon-substituted aziridines contain a more- " S_N1 -susceptible" carbon atom and a more " S_N2 -susceptible" carbon atom depending upon substitution. Thus, the greater the nucleophilicity of the attacking species, the greater will be the proportion of product derived from attack at the more S_N2 -susceptible carbon atom. Changes in the reaction conditions may be expected to increase the rate of the S_N1 or S_N2 reaction and will thus alter the isomer distribution. For example, 3-aryl-2-arylaziridines produce a greater proportion of the α -chloroketone when they react with HCl in the presence of excess chloride ions, than in HCl alone.

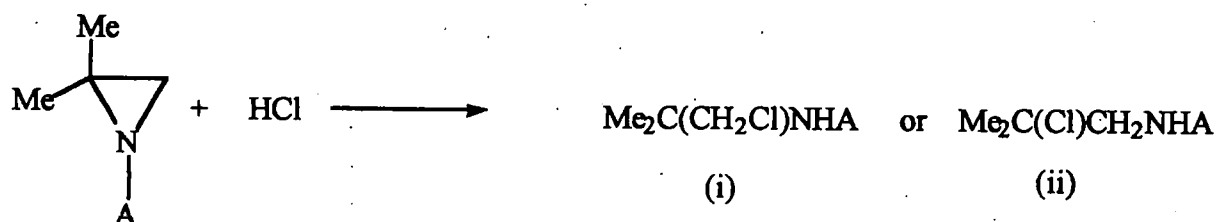
For carbon-substituted activated aziridines, ring opening may also occur via an S_N1 mechanism. This is especially true of 2,2-dialkyl derivatives. Since kinetic and stereochemical evidence (such as is available for basic aziridines) is lacking for the activated aziridines, the most frequently used criterion for identifying the mechanism is the formation of a product derived from attack at the more highly substituted carbon atom. Since activated aziridines react with nucleophiles in the absence of acid, further support of an S_N1 ring-opening is possible where the nature of the predominant isomer changes from acidic or neutral to basic conditions, as in the alcoholysis of 1-benzene sulphonyl-2,2-dimethylaziridine⁷. (Scheme 4.8)



Scheme 4.8

In this case, the rate of the S_N2 process is markedly increased by increasing the nucleophilicity of the attacking species from ROH to RO^- .

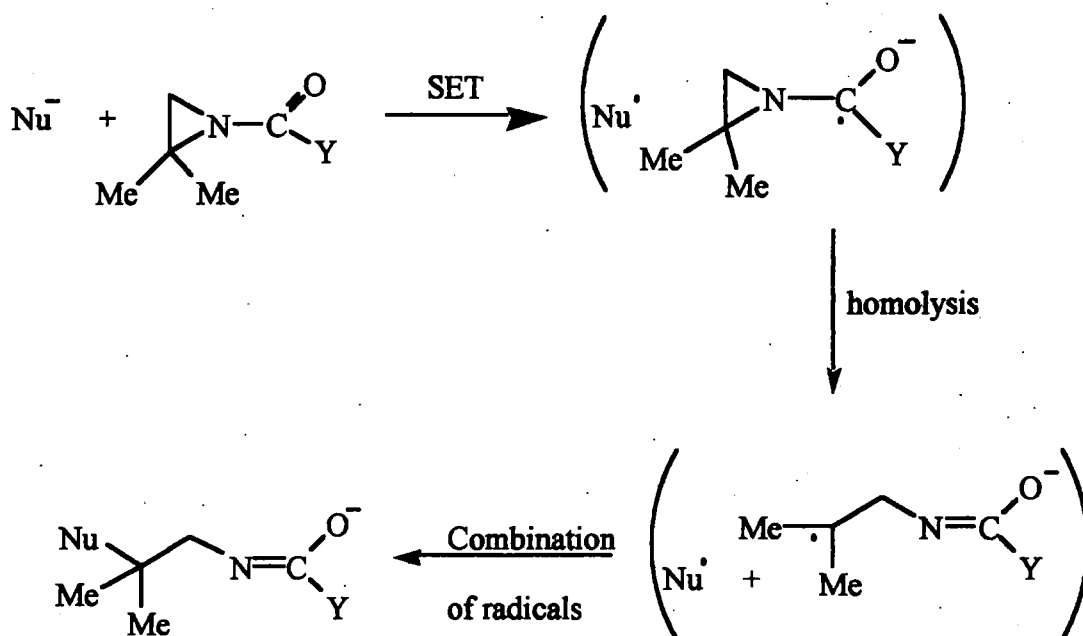
It has been suggested that activated aziridines have a greater tendency to ring open by an S_N1 process than the protonated forms of the corresponding basic aziridine⁸. For example, in Scheme 4.9 when the substituent A on the nitrogen is a hydrogen, the main product is (i),^{4b} but when the substituent on the nitrogen is $PhNHCS^9$ or $PhSO_2^8$, (ii) predominates.



Scheme 4.9

For carbon-unsubstituted activated aziridines, ring-opening solvolysis (or reaction with hydrogen halides) may be considered to be an S_N2 process under either acidic, basic or neutral conditions.

The regioselectivity of nucleophilic attack on activated 2,2-dimethylaziridines also depends on the degree of activation. In highly activated aziridines (e.g. presence of N-sulphonyl groups), attack occurs at the methylene carbons, giving S_N2 -like normal ring opening. However, with less activated (e.g. acyl, dinitrophenyl) aziridines, it occurs at the tertiary carbon (S_N1 -like). This latter "abnormal" ring opening is thought to follow a single electron transfer mechanism (SET)¹⁰. An example of this is the reaction of N-acyl aziridines with the trityl anion as depicted in Scheme 4.10¹¹.



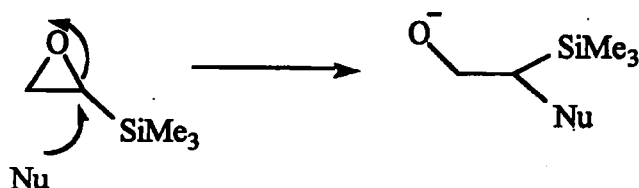
Scheme 4.10

The first step is probably rate determining and may include formation of a molecular complex. The radical anion formed in this step is termed “ketyl” because the carbonyl function of an acyl aziridine resembles a ketone rather than a carboxamide. Subsequent ring homolysis forms the radicals, which then combine to form the product. The normal reaction of such 2,2-dialkylaziridines resembles an $\text{S}_{\text{N}}2$ nucleophilic substitution in the neopentyl position, which would otherwise be slow. With low activation at the nitrogen, such a process will be extremely slow, enabling SET to occur.

4.3 Ring opening reactions of silyl epoxides

Ring-opening reactions of silyl-substituted three-membered ring heterocycles have only been extensively reported for epoxides. Nozaki, Hudrlik and Whiteman¹² have shown that

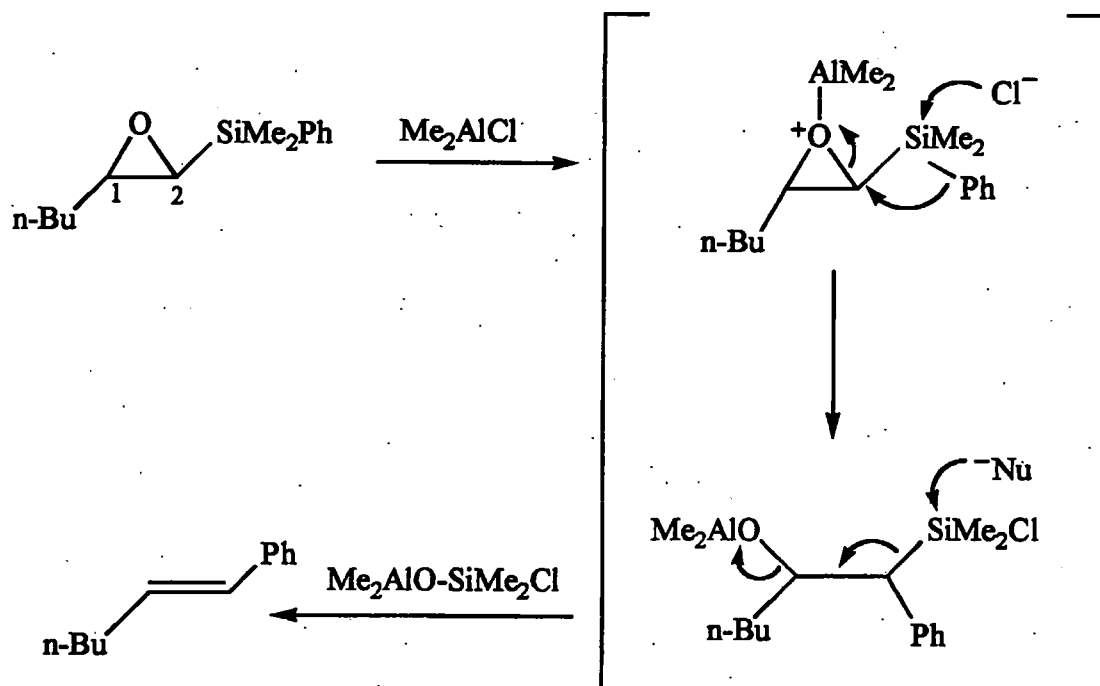
shown that with simple unsubstituted epoxides, attack generally occurs at the carbon α to the silicon accompanied by α -opening of the epoxide ring, Scheme 4.11.



Scheme 4.11

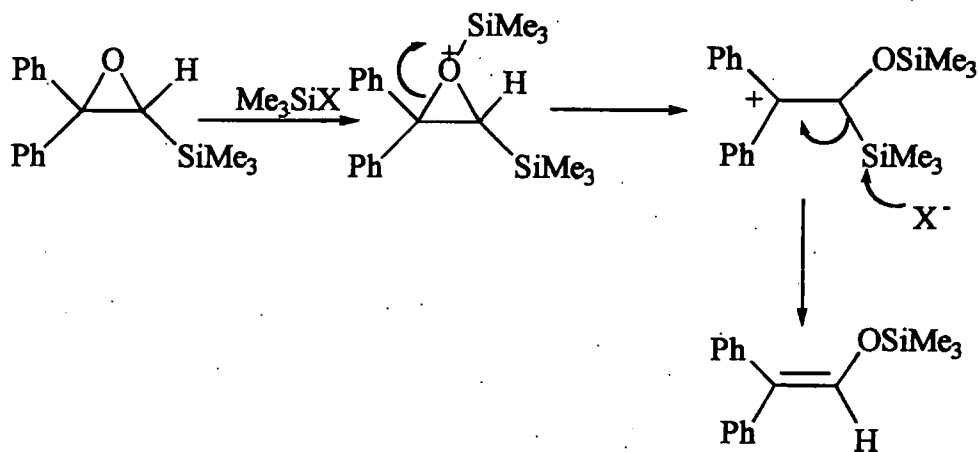
With conformationally rigid or substituted silyl epoxides, nucleophilic attack may result in a mixtures of products arising from cleavage of both C₁-O and C₂-O bonds¹³.

Fleming¹⁴ has shown that the silyl group can be attacked in the presence of a Lewis acid (Scheme 4.12) and both silyl and oxygen groups are eliminated (Peterson reaction)



Scheme 4.12

Soobramanien¹⁵ considered the ring opening reactions of silyl epoxides with various trimethylsilyl halides and trimethylsilyl pseudohalides. She observed that in substituted epoxides like 1-phenyl-2-trimethylsilylepoxide and 1,1-cyclohexyl-2-trimethylsilylepoxide, attack occurred at the carbon α to silicon even in the presence of poor nucleophiles. However with 1,1-diphenyl-2-trimethylsilylepoxide, cleavage occurs at the carbon β to silicon, Scheme 4.13.

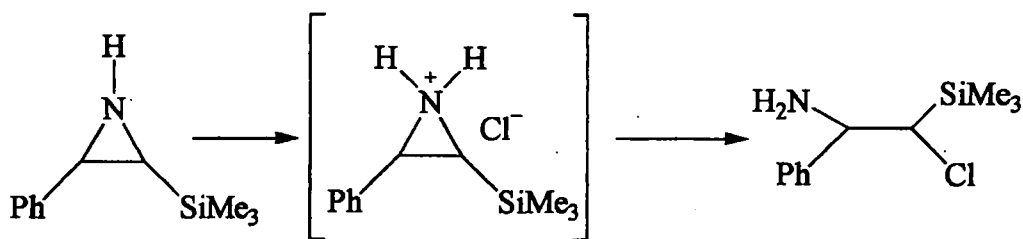


Scheme 4.13

The only explanation for this favoured β cleavage, is that the presence of two phenyl groups on the β carbon can better accommodate a positive charge by conjugation in the transition state and hence overcome the directing effect of the trimethylsilyl group.

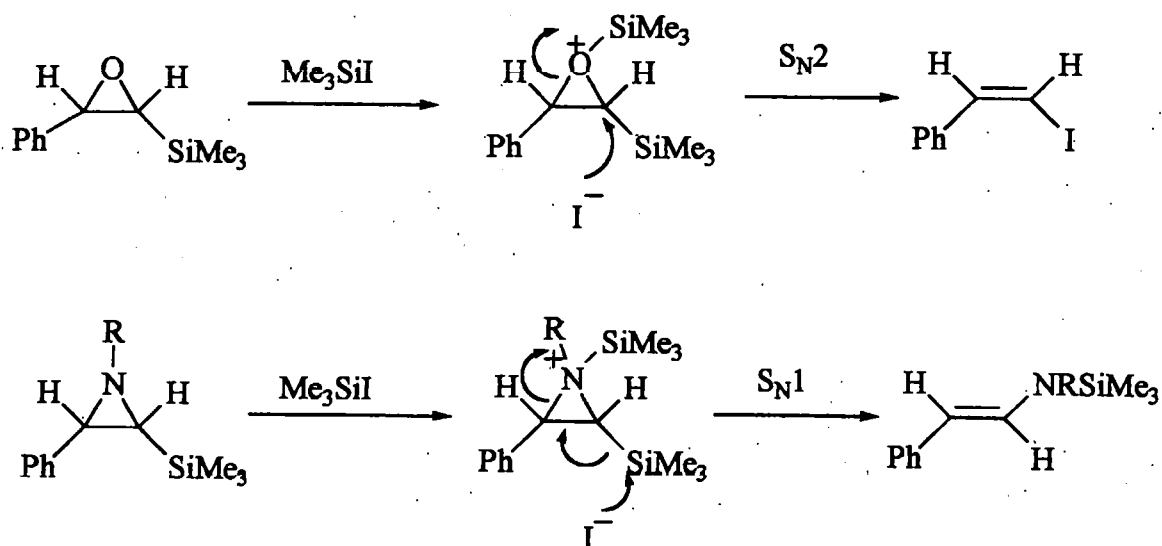
4.4 Ring opening reactions of α -trialkylsilyl aziridines

Both Soobramanien¹⁵ and Kyle¹⁶ have shown that the ring opening reactions of α -silylaziridines are analogous to those of α,β -epoxysilanes. That is, the silicon directs nucleophilic attack to the α position (Scheme 4.14)



Scheme 4.14

However, they did observe a difference in reactivity towards trimethylsilyl iodide between 1-phenyl-2-trimethylsilyl epoxide and the corresponding aziridine, Scheme 4.15.



Scheme 4.15

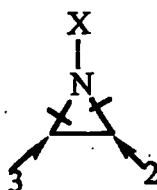
This clearly indicates that the $[NRSiMe_3]^+$ group is more electron-withdrawing than the $[OSiMe_3]^+$ group, hence it leads to an " S_N1 "-type process in the case of silylaziridines. From the reaction systems they studied it was evident that the silyl-substituted aziridines were less reactive than the corresponding α,β -epoxysilanes. Such a difference is not unexpected in view of the greater electronegativity of the oxygen atom. In view of this

rich chemistry, we extended the work further by considering the ring opening reactions of β -trialkylsilyl aziridines.

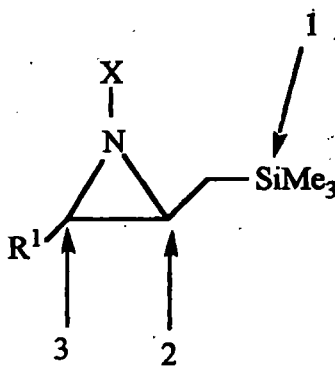
4.5 Results and discussions

4.5.1 Ring-opening reactions of some simple β -trialkylsilyl aziridines

As has already been mentioned, most ring-opening reactions may be formulated as substitutions involving attack of a nucleophile at an aziridine carbon, resulting in the breaking of a C-N bond.



However, with β -trialkylsilyl aziridines, attack could also occur at the silicon-group.

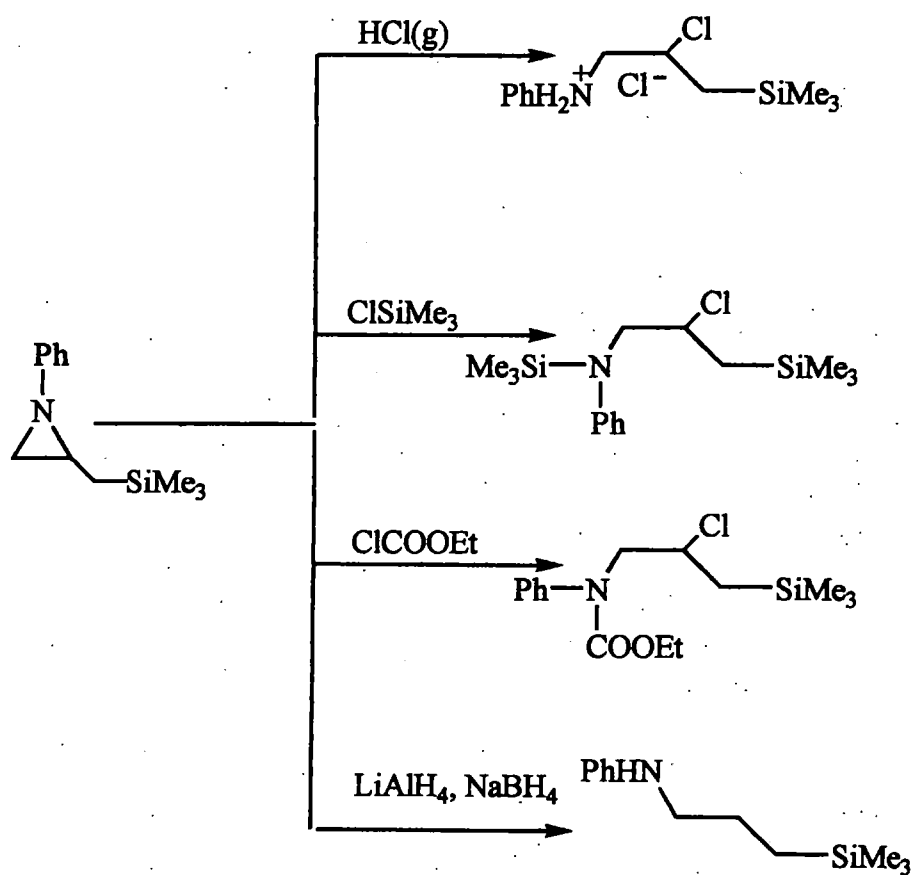


The β -trialkylsilyl aziridines were reacted with the following reagents shown in Table 4.1

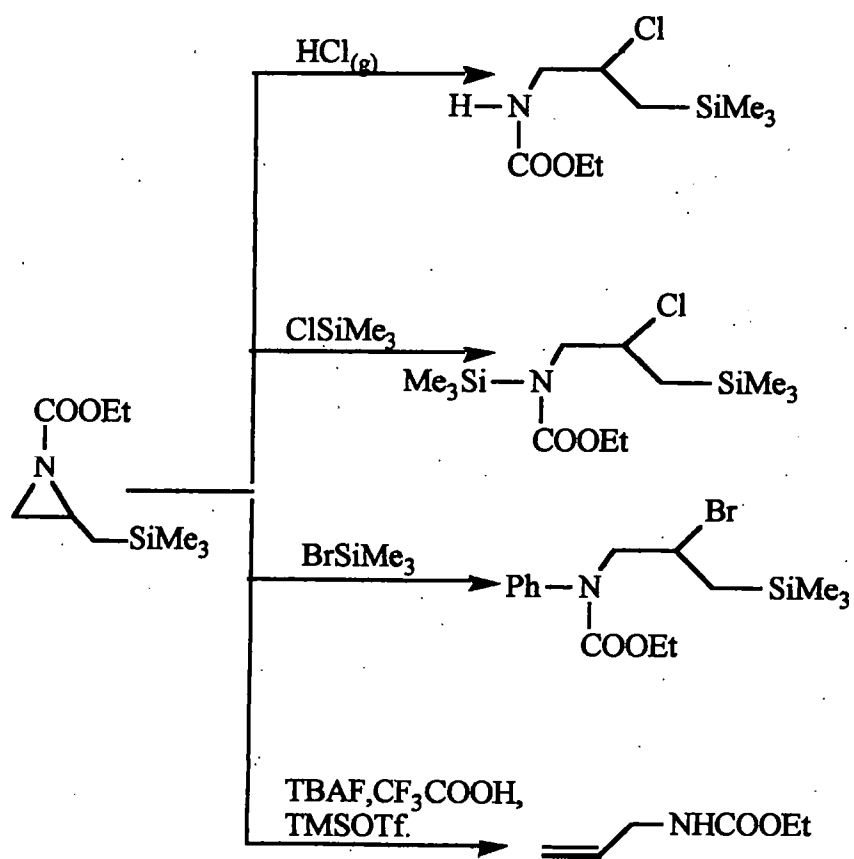
Table 4.1

	Reagent Name	Formula	Nucleophilic Species
1	Hydrogen chloride gas	HCl	Cl ⁻
2	Trimethylsilyl chloride	(CH ₃) ₃ SiCl	Cl ⁻
3	Ethyl chloroformate	ClCO ₂ Et	Cl ⁻
4	Morpholine	O(CH ₂)NH	O(CH ₂)N ⁻
5	Phenol	PhOH	PhO ⁻
6	p-Cresol	CH ₃ C ₆ H ₄ OH	CH ₃ C ₆ H ₄ O ⁻
7	Sodium azide	NaN ₃	N ₃ ⁻
8	Lithium aluminium hydride	LiAlH	H ⁻
9	Thiophenol	PhSH	PhS ⁻
10	Sodium methoxide	NaOMe	MeO ⁻
11	Sodium Phenolate	PhONa	PhO ⁻
12	Sodium thiophenolate	PhSNa	PhS ⁻
13	Sodium Borohydride	NaBH ₄	H ⁻
14	Organometallic reagents	RMgX	R ⁻
15	Tetrabutyl ammonium fluoride	[CH ₃ (CH ₂) ₃] ₄ NF	F ⁻
16	Trimethylsilyl triflate	CF ₃ SO ₂ (SiCH ₃) ₃	CF ₃ SO ₂ ⁻
17	Borontrifluoride etherate	BF ₃ OEt	EtO ⁻

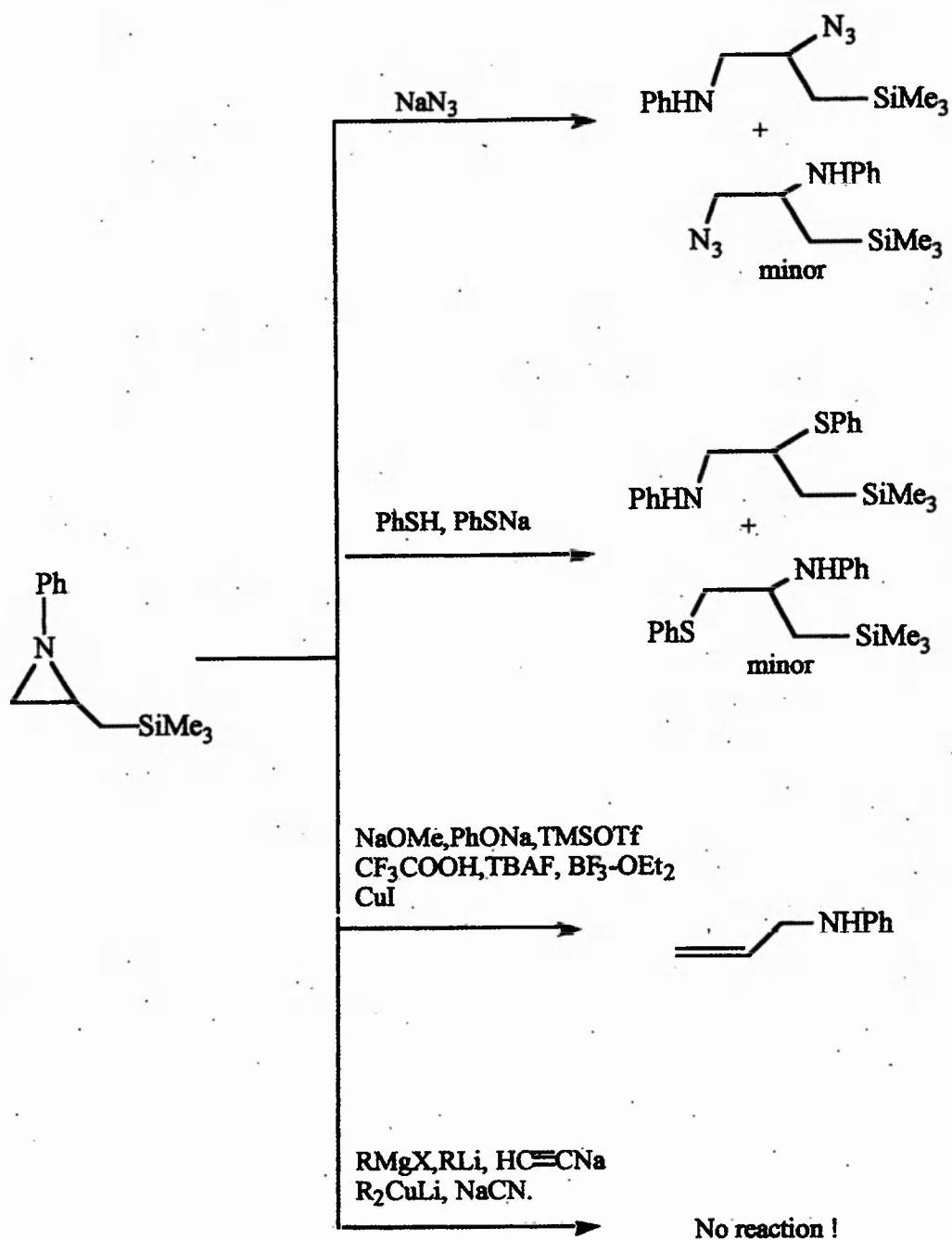
The reactions above are summarized in Schemes 4.16, 4.17 and 4.18 below. They are discussed separately, in the subsections that follow, on the basis of the element, which becomes attached to the carbon atom in the newly formed compound.



Scheme 4.16



Scheme 4.17



Scheme 4.18

4.5.2. Formation of a Carbon-Halogen bond (C-X) in the product

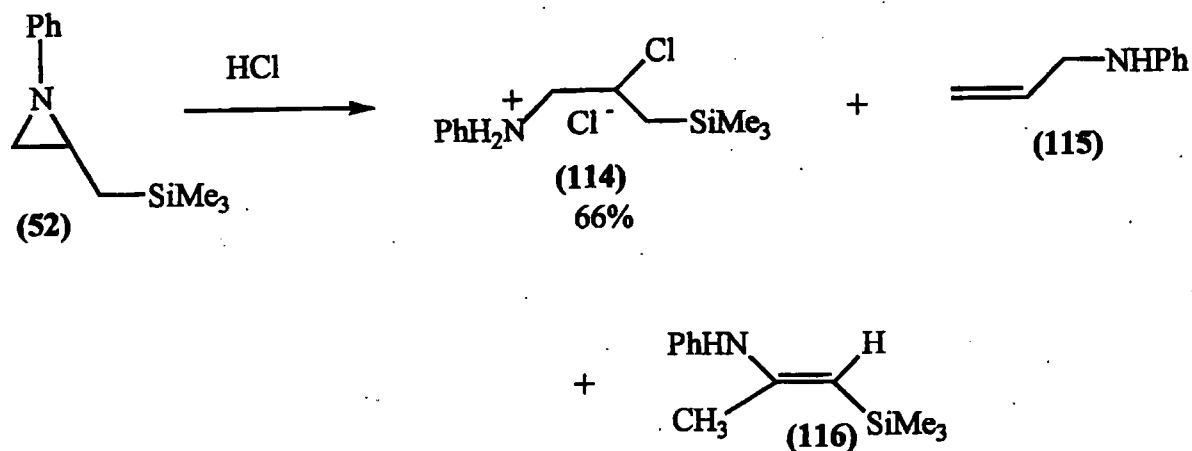
The following reagents were employed which form a C-X bond in the ring-opened compounds, where X= Cl or Br.

- (i). Hydrogen chloride gas
- (ii). Hydrogen bromide gas
- (iii). Trimethylsilyl chloride
- (iv). Ethyl chloroformate
- (v). Acetyl chloride.

A typical reaction involves the dropwise addition of an equimolar amount of the reagent to a solution of silyl-substituted aziridine in deuterated chloroform in a 5mm n.m.r. tube at room temperature. Alternatively, a gas was passed through a solution of the aziridine in ether-benzene. An explanation for the formation of such compounds will be based upon a typical reaction, that of hydrogen chloride with N-phenyl-2-methyltrimethylsilyl aziridine.

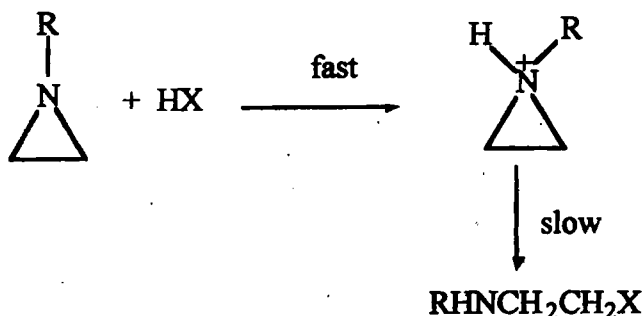
4.5.2.1. Ring-opening reactions of β -trialkylsilylaziridines with hydrogen halide gas (formation of C-Cl bond).

Reaction of N-phenyl-2-trimethylsilylmethylaziridine **52** with hydrogen chloride gas in a benzene-ether solution, gave predominantly the addition product **114** after removal of excess solvent. However a trace amount of allylamine **115** and an alkene, identified by nmr as possibly **116**, was observed as shown in Scheme 4.19.



Scheme 4.19

The reaction of an aziridine with a halogen acid can be regarded as the reaction of a halide ion with an intermediate aziridinium salt (Scheme 4.20)¹⁷

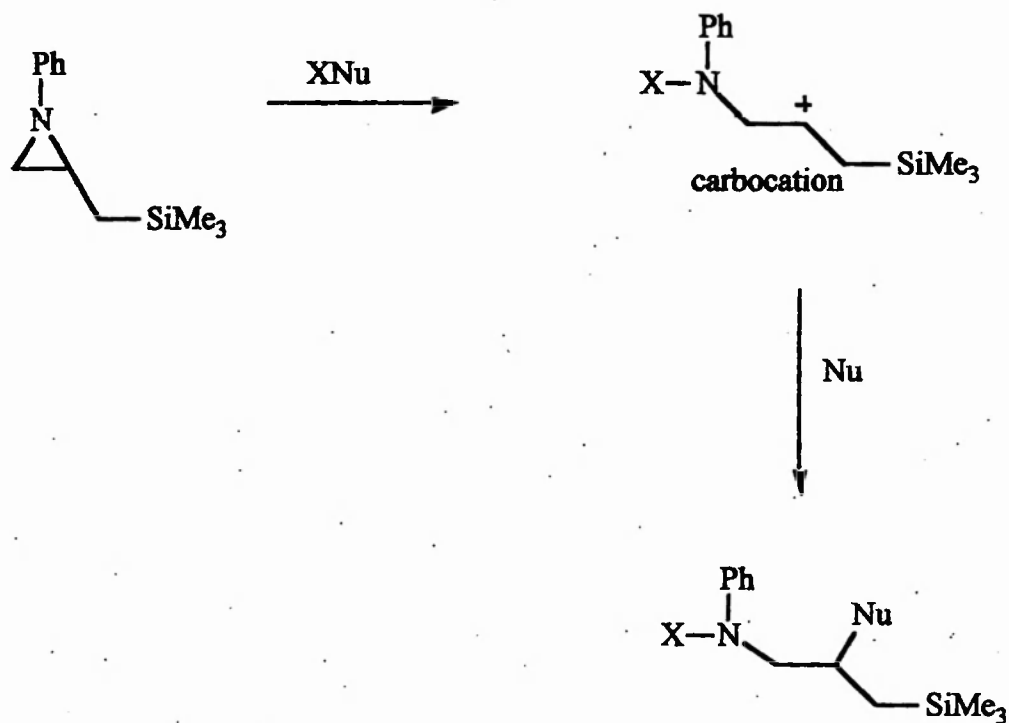


Scheme 4.20

The products formed suggest the involvement of a predominantly “S_N1”-type mechanism, in which the halide ion becomes attached to the carbon most likely to accommodate a positive charge.

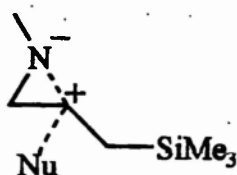
With our aziridines, the halide becomes attached to the carbon β-to silicon, despite being the most sterically hindered site. By an “S_N1”-type process, we do not necessarily mean the

formation of an open chain secondary carbocation followed by attack of the nucleophile (Scheme 4.21),

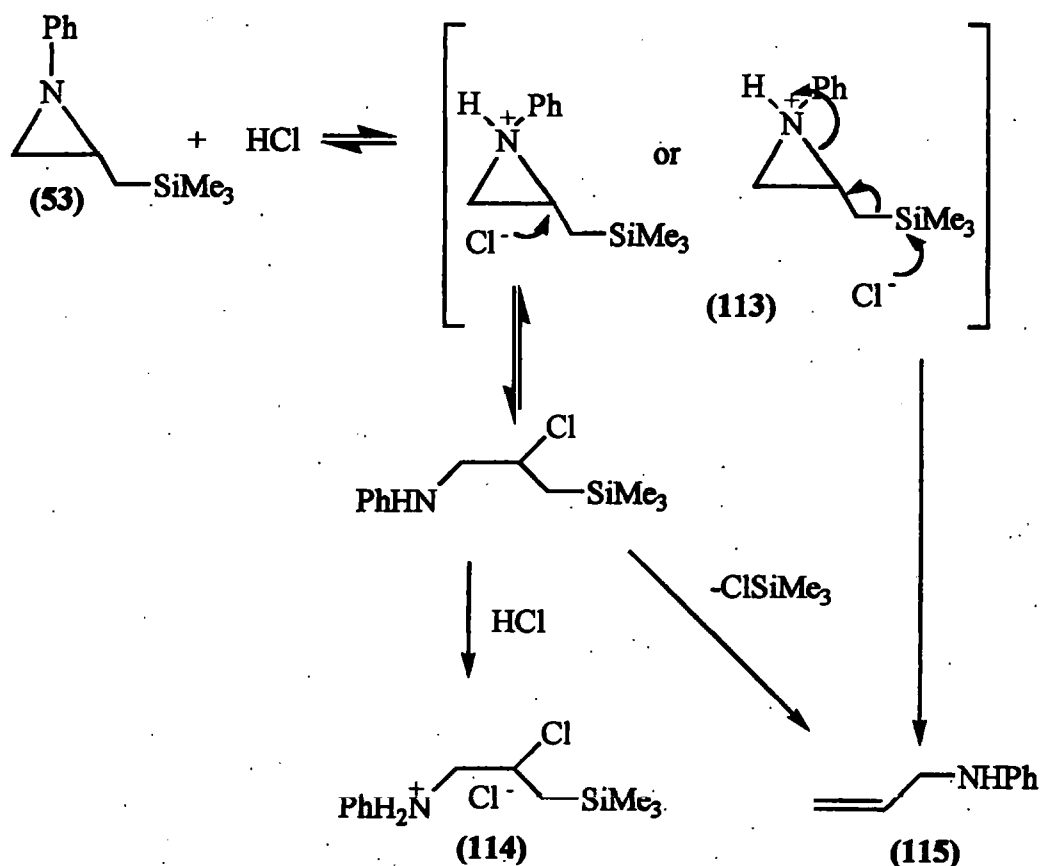


Scheme 4.21

but rather, the formation of a transition state, with a large amount of carbocationic character on the β -carbon, which is stabilised by the C-Si bond (hyperconjugation).



The allylamine could be formed by a loss of ClSiMe_3 from the ring-opened product or by direct nucleophilic attack on silicon. Scheme 4.22 summarizes the processes involved in the reaction of N-phenyl-2-methyltrimethylsilylaziridine with hydrogen chloride gas.

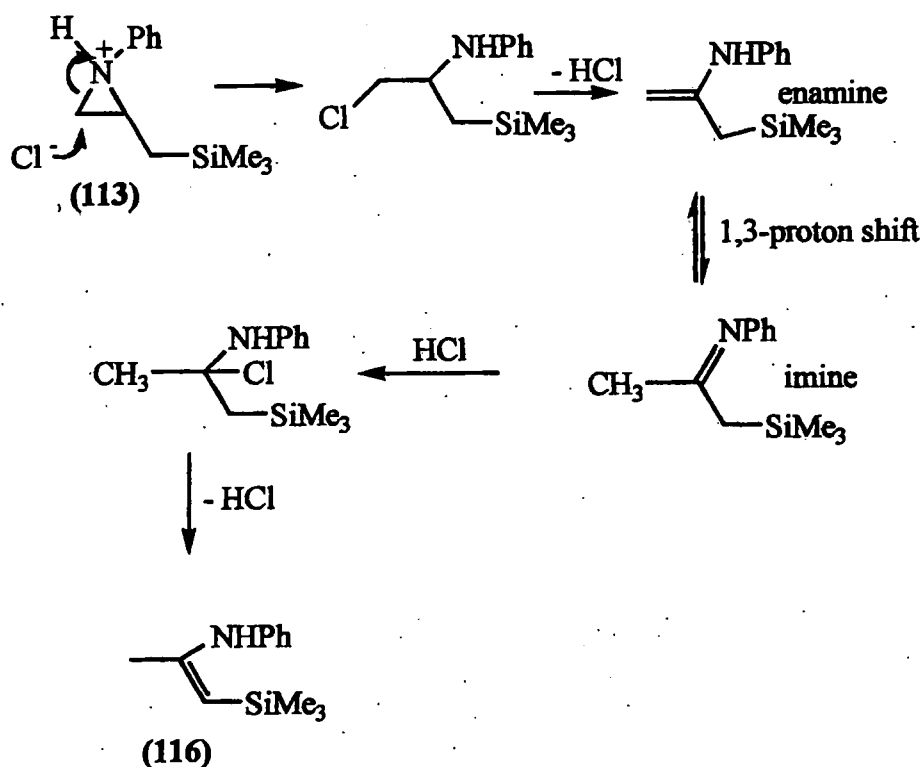


Scheme 4.22

As with other aziridines, the first step is protonation of the aziridine to form the intermediate aziridinium salt, which could not be isolated as a result of rapid ring opening β - cleavage (path a) to give the β -chlorosilyl amine, which reacted further with excess hydrogen chloride to give the isolatable product 116. The formation of the allylamine 115

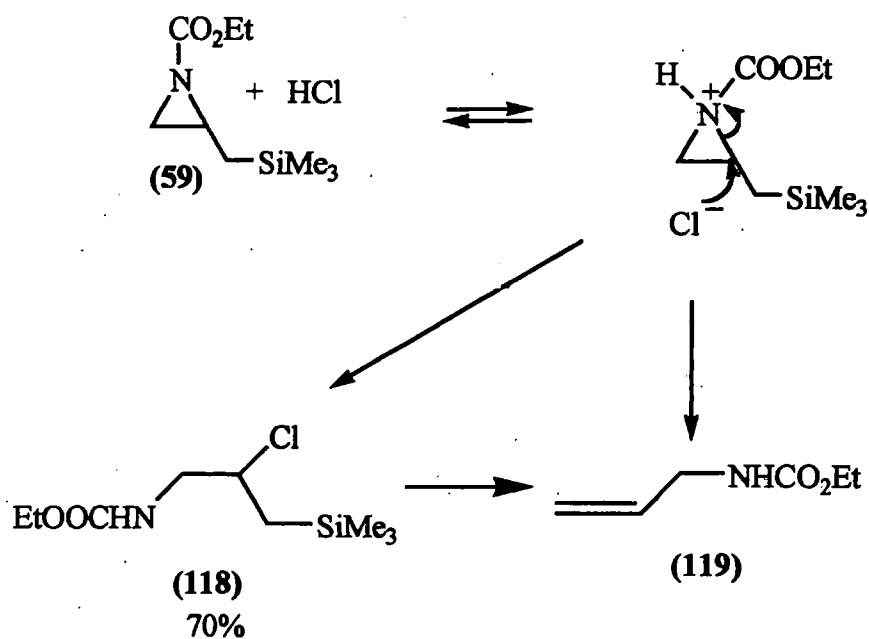
could be from the direct nucleophilic attack on the trimethylsilyl group of the intermediate or from the β -haloamine.

Cleavage at the γ carbon, via an " S_N2 "-type process occur, only to a small extent. This leads to an unstable addition product, which loses HCl to form an enamine. Under our reaction condition, the enamine formed undergoes a 1,3-proton shift to give the imine (enamine-imine tautomerism). Further addition of HCl followed by elimination gave the alkene **116** (Scheme 4.23) which was only identified in trace amounts by NMR.



Scheme 4.23

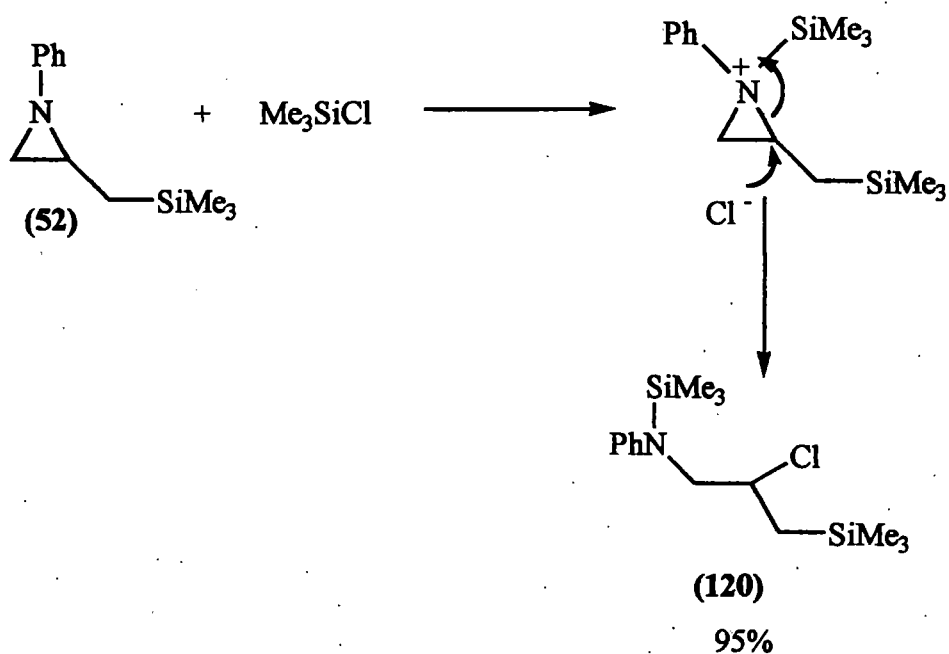
N-carboethoxy aziridine **58** reacted similarly with hydrogen chloride gas to give predominantly the β -addition product **118** and the allylamine **119**, but in this case all attempt to isolate the addition product led to decomposition to the allylamine (Scheme 4.24)



Scheme 4.24

4.5.2.2 Reaction of silyl-aziridines with trimethylsilylhalides and pseudohalides.

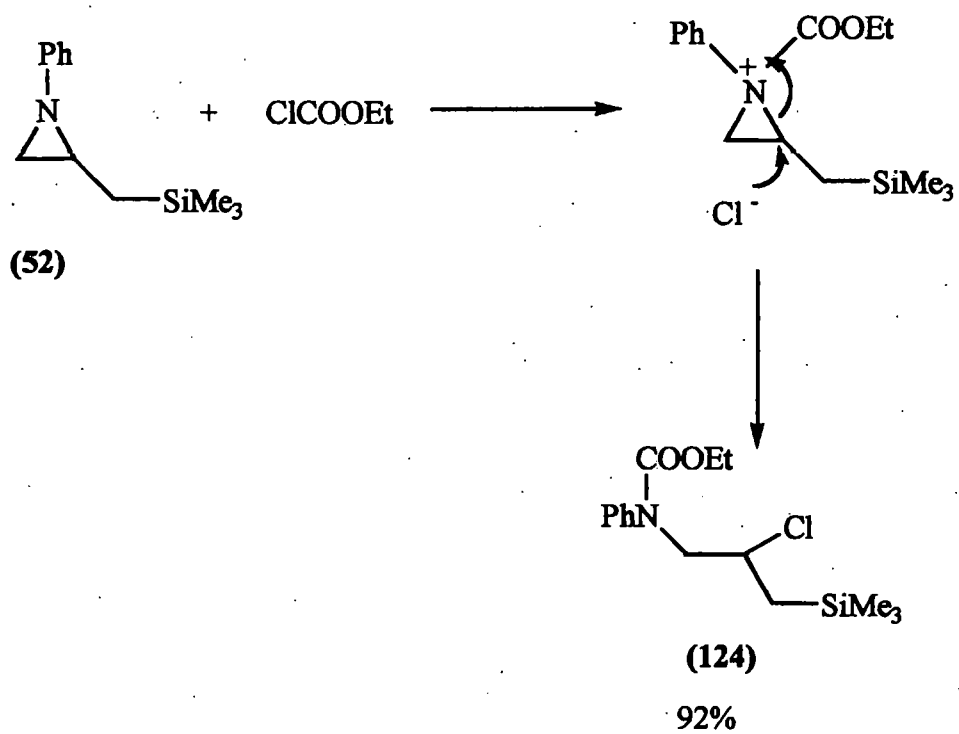
β -trialkylsilyl aziridines reacted with trimethylsilyl chloride and trimethylsilyl bromide to give mainly the addition product. The reaction of the silyl-aziridine 52 with trimethylsilyl chloride is representative and is shown in Scheme 4.25.



Scheme 4.25

The addition product **120** results from the initial attack of the nitrogen lone pair on the silicon atom of the trimethylsilyl chloride to form the intermediate quaternary salt. Cleavage of the C-N bond via an “ S_N1 ”-type process gave quantitatively only the β -addition product.

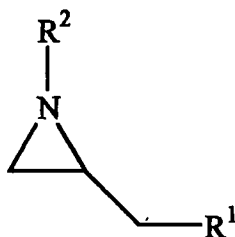
Similarly, ethylchloroformate reacted with N-phenyl-2-methyltrimethylsilyl aziridine **52**, to give only the β -addition product **124** Scheme 4.26.



Scheme 4.26

Table 4.1

Summary of the formation of Carbon-Halogen bonds from silyl-substituted aziridines of the type:



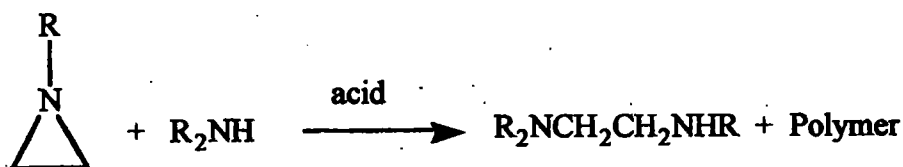
Aziridine			Reagent	Ring-opened compounds		
R¹	R²			Formulae		%Yield
52	SiMe₃	Ph	HCl(g)	116	Me₃SiCH₂(Cl)CH-CH₂NH₂⁺Ph Cl⁻	66 ¹
55	SiMe₂Ph	Ph	HCl(g)	117	PhMe₂SiCH₂(Cl)CH-CH₂NH₂⁺Ph Cl⁻	85 ²
58	SiMe₃	CO₂Et	HCl(g)	118	Me₃SiCH₂(Cl)CH-CH₂NH₂CO₂Et Cl⁻	70 ²
52	SiMe₃	Ph	ClSiMe₃	120	Me₃SiCH₂(Cl)CH-CH₂NPh(SiMe₃)	95 ²
55	SiMe₂Ph	Ph	ClSiMe₃	121	PhMe₂SiCH₂(Cl)CH-CH₂NPh(SiMe₃)	60 ²
58	SiMe₃	CO₂Et	ClSiMe₃	122	Me₃SiCH₂(Cl)CH-CH₂NCO₂Et(SiMe₃)	70 ²
58	SiMe₃	CO₂Et	BrSiMe₃	123	Me₃SiCH₂(Br)CH-CH₂NCO₂Et(SiMe₃)	50 ²
52	SiMe₃	Ph	ClCO₂Et	124	Me₃SiCH₂(Cl)CH-CH₂NPh(CO₂Et)	92 ²

1 = yield of isolated product

2 = determined from nmr without isolation

4.5.3. Ring-opening reactions of β -trialkylsilylaziridines with nitrogen nucleophiles (formation of a C-N bond).

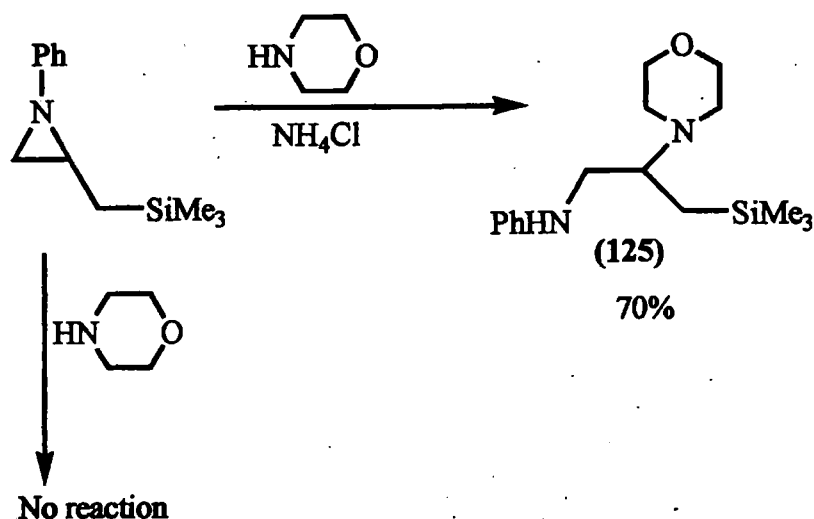
Ammonia and amines have been shown to react with aziridines in the presence of acid catalysts to give diamines and other polymeric products¹⁸. The general reaction is shown in Scheme 4.27



Scheme 4.27

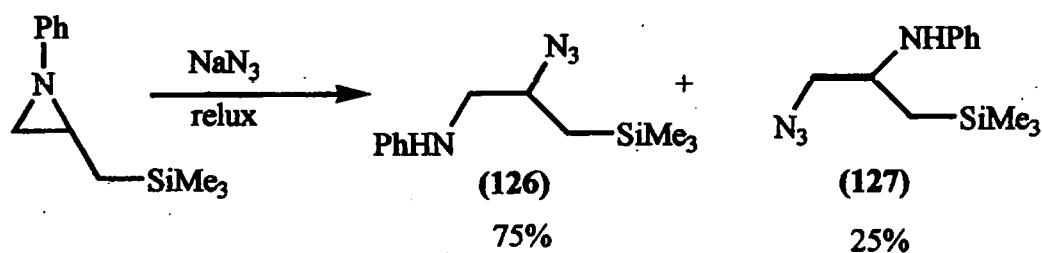
The reaction occurs more readily with N-sulfonyl aziridines, because electron-withdrawal by the sulfonyl group makes the aziridine carbons more susceptible to nucleophilic attack. We examined the ring opening reaction of β -trialkylsilyl aziridines with morpholine and sodium azide. The morpholine only reacted in the presence of ammonium chloride to give the ring opened product.

In a typical run, an equimolar amount of the silyl-aziridine and the morpholine were refluxed for 10hrs in carbon tetrachloride in the presence of a catalytic amount of ammonium chloride. This gave predominantly the β -addition product 125 and other unidentified polymeric products. The regiochemistry of the products indicates that the ring-opening occurs via an " S_N1 "-type process as earlier observed with hydrogen chloride gas. The ammonium chloride protonates the aziridine and the amine attacks at the β -carbon as expected, Scheme 4.28.



Scheme 4.28

With sodium azide, in the absence of any acid catalysis, ring-opening occurred to give a mixture of two isomers 126 and 127 in which the major product was found to be 126 with an isomer ratio of 3:1. This product distribution, suggests that both “ $\text{S}_{\text{N}}1$ ”-type and “ $\text{S}_{\text{N}}2$ ”-type processes are taking place, with the former process dominating (Scheme 4.29).

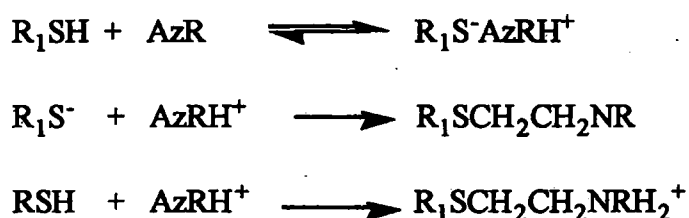


Scheme 4.29

Since azide is a good nucleophile, it is not surprising that the “ $\text{S}_{\text{N}}2$ ”-type product starts to become more important. The implication for the “ $\text{S}_{\text{N}}1$ ”-type process is that, with the better nucleophiles, there is less positive charge build up on the β -carbon in the transition state so that hyperconjugation is less important in distinguishing between the two carbons.

4.5.4. Ring-opening reactions of β -trialkylsilylaziridines with sulphur nucleophiles (formation of a C-S bond).

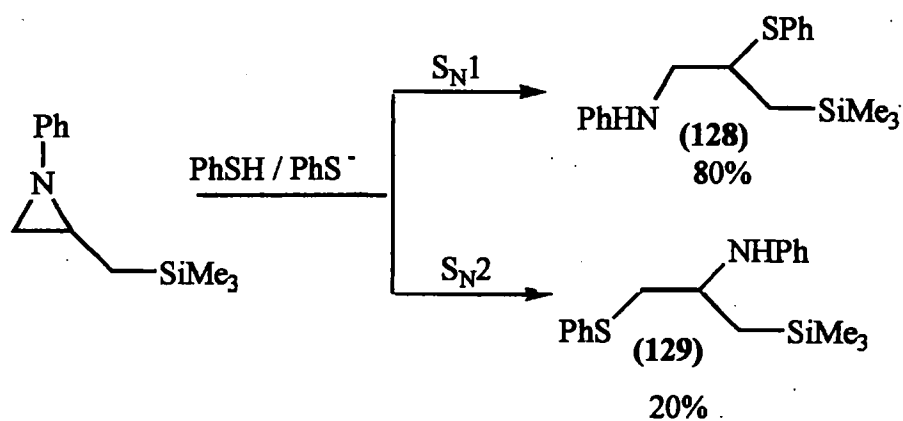
A number of methods have been used for the synthesis of compounds of the type $R_2NCH_2CH_2SH$, among them are the displacement of chloride ion from a β -aminoethyl chloride with sodium hydrosulfite and the reduction of a Schiff base. One of the most important preparative methods is the ring-opening of aziridines with sulfur nucleophiles such as hydrogen sulfide¹⁹, mercaptans²⁰ and thiophenols²¹. A typical reaction scheme for the ring-opening of aziridines with sulphur nucleophiles is shown in the Scheme 4.30.



Scheme 4.30

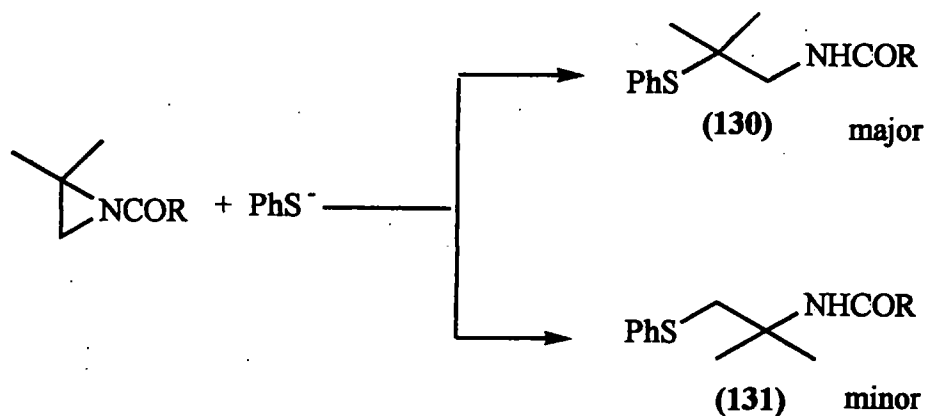
The RS^- (and / or RSH) is sufficiently nucleophilic to compete successfully for the protonated aziridine with any free amino group (aziridine or ring-opened product) present in the medium. Thus, it is unnecessary to employ large amounts of acid or a large excess of RSH compound.

In our work to form β -aminothiols, we refluxed an equimolar amount of N-phenyl silylaziridine with thiophenol in carbon tetrachloride for 10hrs. The product isolated was found to be a mixture of two isomers 128 and 129, with the major isomer (ratio 3:1) being 128. Repeating the above reaction with sodium thiophenolate ($PhSNa$) did not alter the product distribution (Scheme 4.31).



Scheme 4.31

Whilst we might expect PhSH to give predominantly **128** as the reagent is slightly acidic, the predominant formation of **129** with the thiophenolate (PhS^-), is more difficult to explain. We would expect the ring-opening to occur via an “ $\text{S}_{\text{N}}2$ ”-type mechanism, with the PhS^- group attacking the less substituted carbon of the ring to give **129**. This ‘abnormal’ observation can only be ascribed to a significant build-up of positive charge in the transition state which is further stabilised by hyper-conjugation. A similar pattern of reactivity has been observed²³ where an N-acylated aziridine reacted with the strong and sterically undemanding thiophenolate ion to give **130** as the major product (Scheme 4.32)

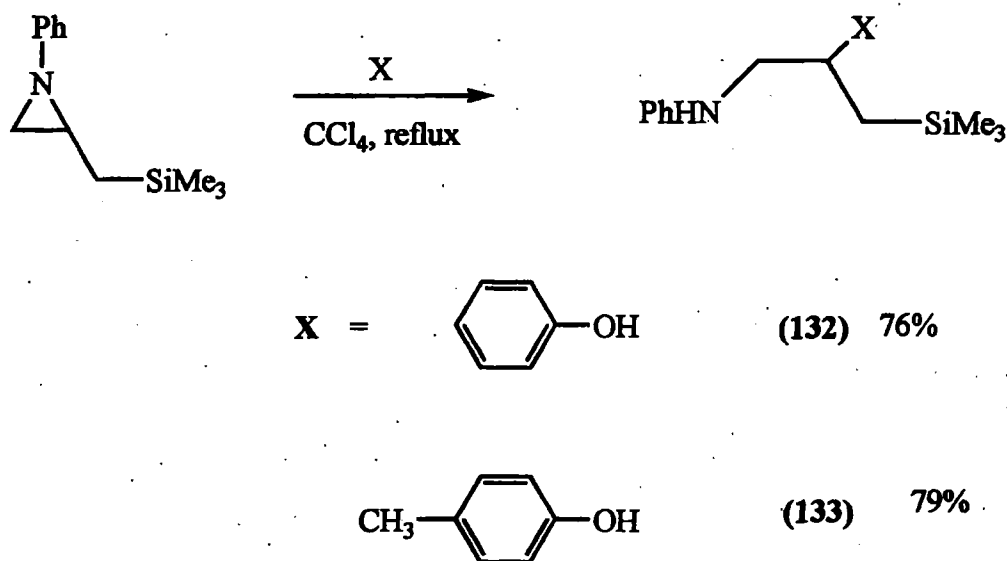


Scheme 4.32

4.5.5 Ring-opening reactions of β -trialkylsilylaziridines with oxygen nucleophiles (formation of a C-O bond).

The acid-catalysed hydrolysis of aziridines is usually of little preparative value. Such a reaction may represent the final step in the isomerization of a β -amino alcohol²².

There are surprisingly few reports describing reactions of phenols with aziridines. We have found that phenol and p-cresol react with the β -silylated aziridines in the absence of any other acid. Refluxing an equimolar amount of N-phenylsilyl aziridine with phenol and p-Cresol in carbon tetrachloride for 10hrs. gave solely the β -addition products 132 and 133 respectively, (Scheme 4.33).

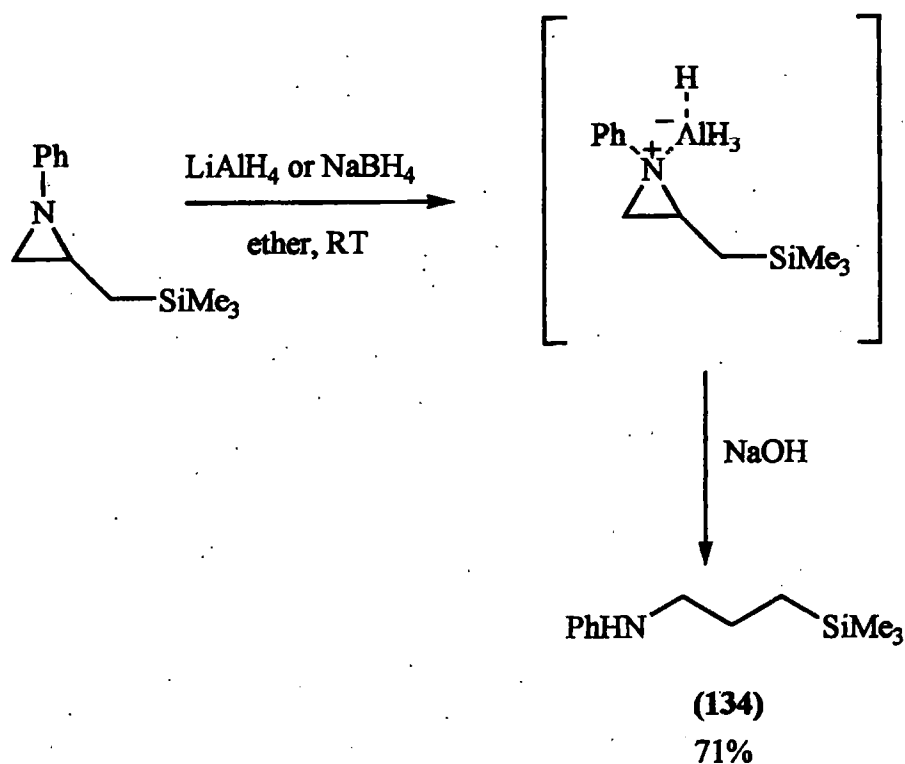


Scheme 4.33

The regiochemistry again infers an " S_N1 "-type mechanism.

**4.5.6. Ring-opening reactions of β -trialkylsilylaziridines with reducing agents
(formation of a C-H bond).**

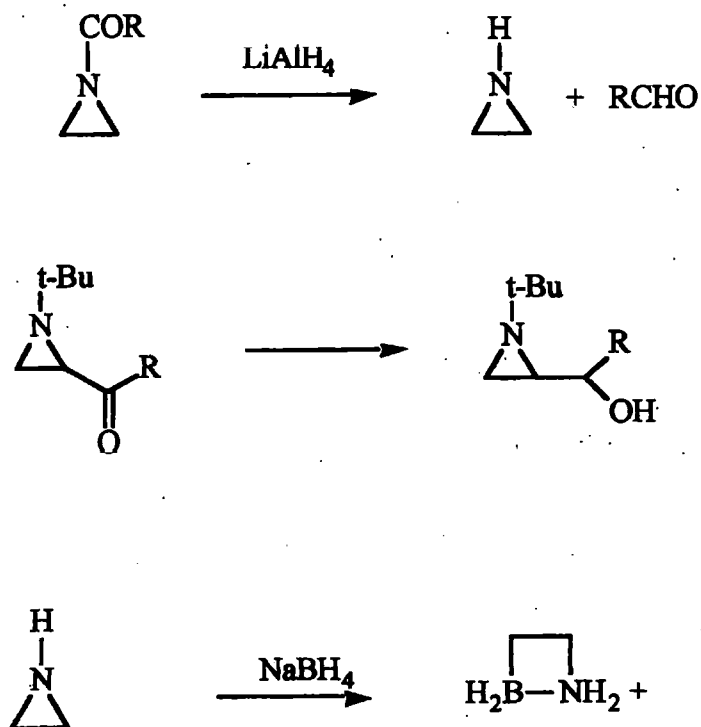
Stirring N-phenylsilyl aziridine in a slurry of lithium aluminium hydride (3mole equivalent) in dry ether at room temperature overnight gave the ring-opened product 134. The regiochemistry, again implies it is formed as a result of an S_N1 -type process. Interestingly, even with sodium borohydride, a similar reaction product was isolated (Scheme 4.34).



Scheme 4.34

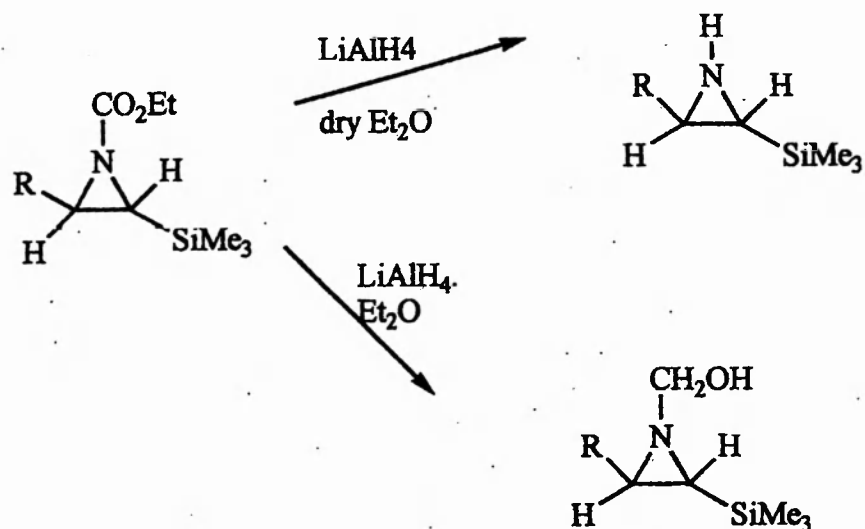
This was unexpected, since the hydrogenolysis of aziridines does not consistently result in the cleavage of the carbon -nitrogen bond. For example, 1-acyl aziridine are reduced to the -NH or the -OH form with lithium aluminiumhydride^{23,24}. A most unusual

reaction between an N- unsubstituted aziridine and sodium borohydride has also been reported²⁵ (Scheme 4.35).



Scheme 4.35

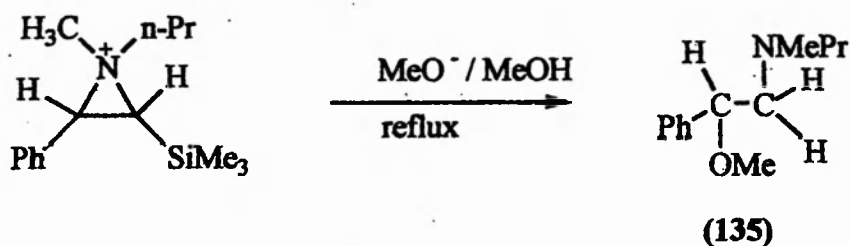
Kyle¹⁶ has reacted 1-carboethoxy-2-trimethylsilyl aziridine with lithium aluminium hydride under different conditions and observed that reaction occurs exclusively at the carbonyl site (Scheme 4.36) with an evidence of ring cleavage.



Scheme 4.36

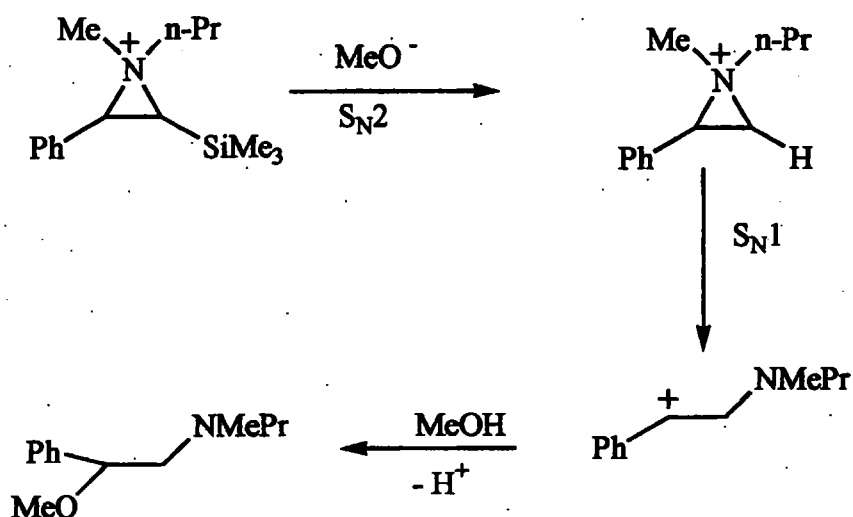
4.5.7 Ring-opening reactions of trialkylsilylaziridines by nucleophilic attack on silicon (formation of allylamines).

The ring-opening of silylated aziridines does not only take place via nucleophilic attack on the aziridine ring. Attack at the silicon resulting in its elimination and subsequent ring-opening can also occur. Methanolysis²⁸ of quaternised silylated aziridines, in the presence of a stoichiometric amount of methoxide ion, gives a ring-opened-product which has lost its silicon (Scheme 4.37).



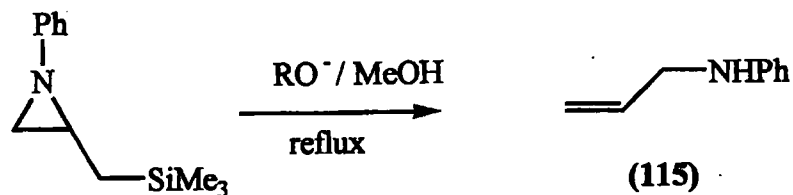
Scheme 4.37

There are a number of possible mechanisms for the reaction of the aziridinium salt with methoxide ion to give 135. The absence of a ring-opened adduct which had not desilylated indicates that desilylation rather than ring-opening is the preferred initial mode of attack of the methoxide ion. Desilylation, therefore, leads to an unsymmetrically carbon-substituted aziridinium salt, which undergoes an "S_N1"-type opening to give a carbonium ion intermediate which is subsequently hydrolysed to 135, Scheme 4.38.



Scheme 4.38

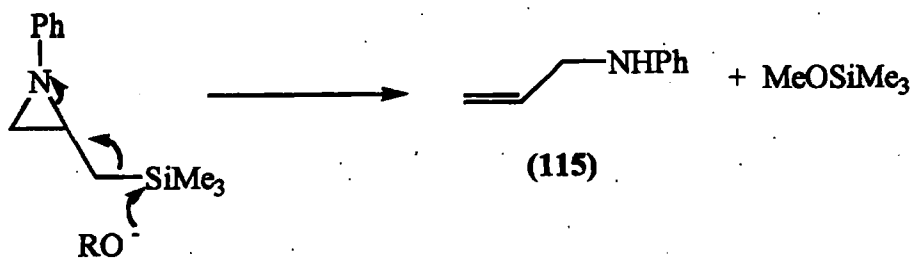
In the presence of a stoichiometric amount of freshly prepared methoxide or phenoxide ion in methanol, β -trialkylsilylaziridines gave allylamine 115 as the only product (Scheme 4.39).



R = Me, Ph

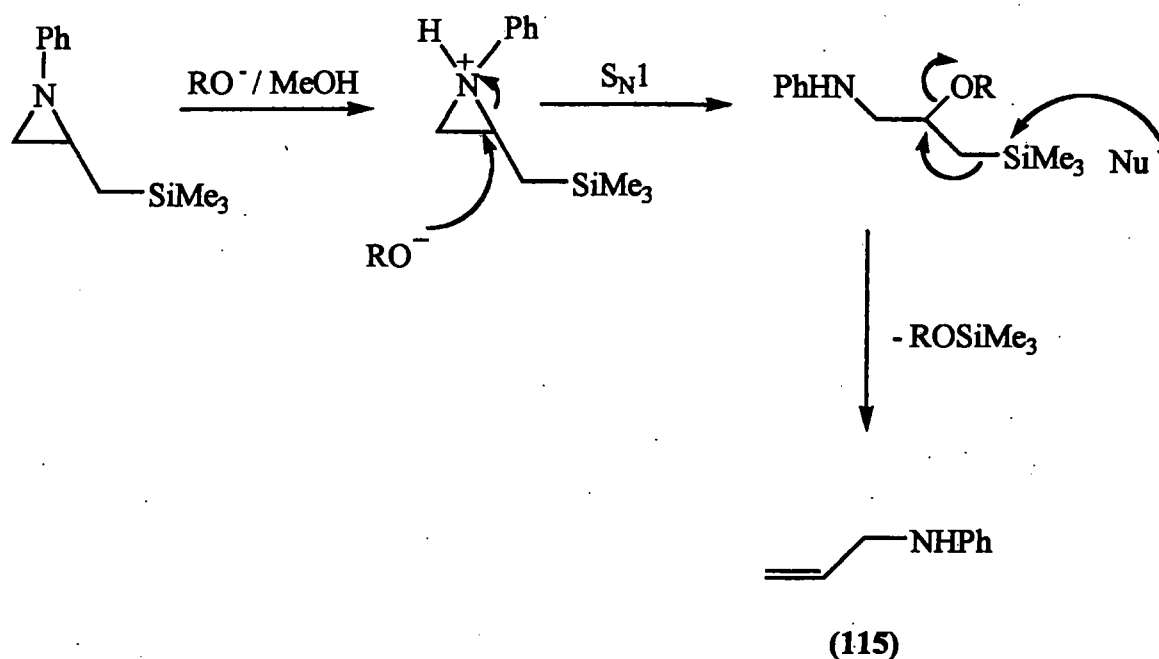
Scheme 4.39

A possible mechanism might involve a direct nucleophilic attack on silicon via an “S_N2”-type process as shown in Scheme 4.40 below:



Scheme 4.40

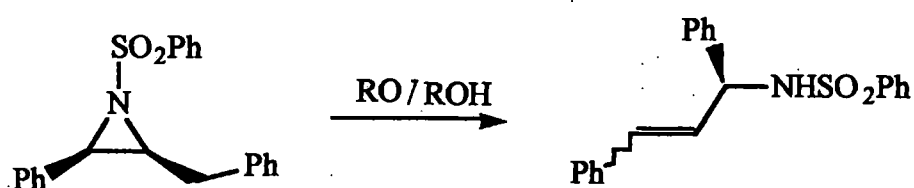
Another possible explanation for the formation of the allylamine is via the formation of the β-addition product in an “S_N1”-type process reaction, which is subsequently converted to the allylamine, Scheme 4.41.



Scheme 4.41

In the case of phenol, the β -addition product was isolated (Scheme 4.33). The absence of a ring-opened product which has not desilylated in this case suggests that both phenoxide and methoxide ions prefer to attack the silicon group, in an " S_N2 "-type process.

In non-silylated allylic systems, it has been shown that a base removes a proton from the allylic position²⁶ to give mainly an allylamine (Scheme 4.42).



Scheme 4.42

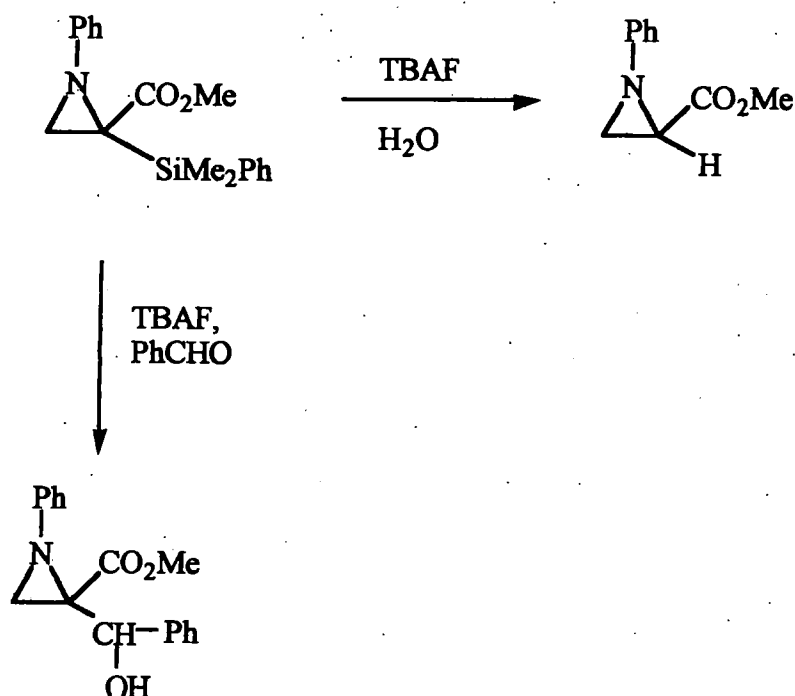
The following reagents all gave allylamine in their reaction with β -trialkylsilyl aziridines.

- (i) Tetrabutylammonium fluoride (TBAF), (ii) Borontrifluoride etherate ($\text{BF}_3 \cdot \text{Et}_2\text{O}$)
(iii) Trifluoromethane sulphonic acid (HOTf), (iv) Trimethylsilyl triflate (TMSOTf)
(v) Trifluoroacetic acid (CF_3COOH), (vi) Copper iodide (CuI)

4.5.7.1. Fluorodesilylation of silylaziridines

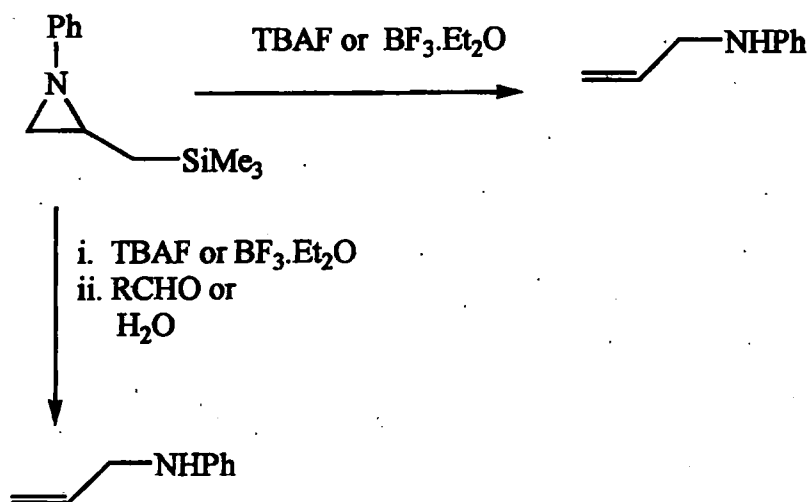
Fluorodesilylation reactions of silylaziridines have received little attention and only few incidence have been reported^{14, 27}. Atkinson²⁷ was the first to successfully desilylate and trap the desilylated aziridine with an electrophile.

After extensive research work, Soobramanien and Kyle successfully desilylated aziridines, using tetrabutylammonium fluoride Scheme 4.43



Scheme 4.43

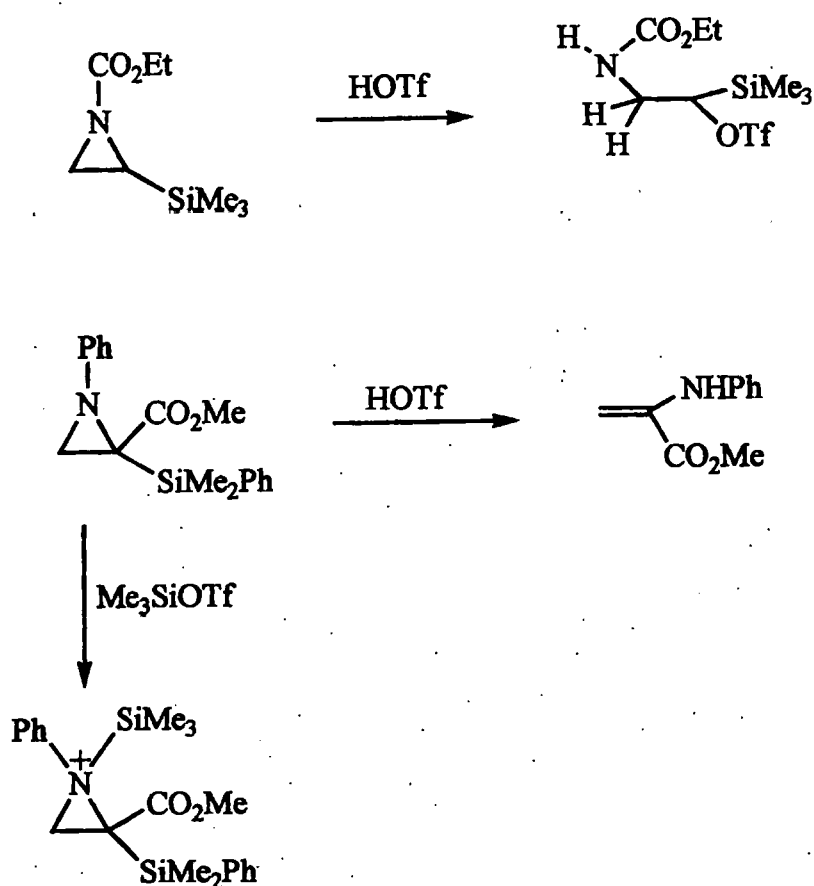
As an extension of this chemistry, we reacted β -trialkylsilylaziridines with tetrabutylammonium fluoride and borontrifluoride etherate. In both cases, no product of desilylation was isolated and all attempts to trap the carbanion, with an electrophile failed. Instead, allylamine was recovered, Scheme 4.44.



Scheme 4.44

4.5.7.2. Ring-opening reactions with triflates

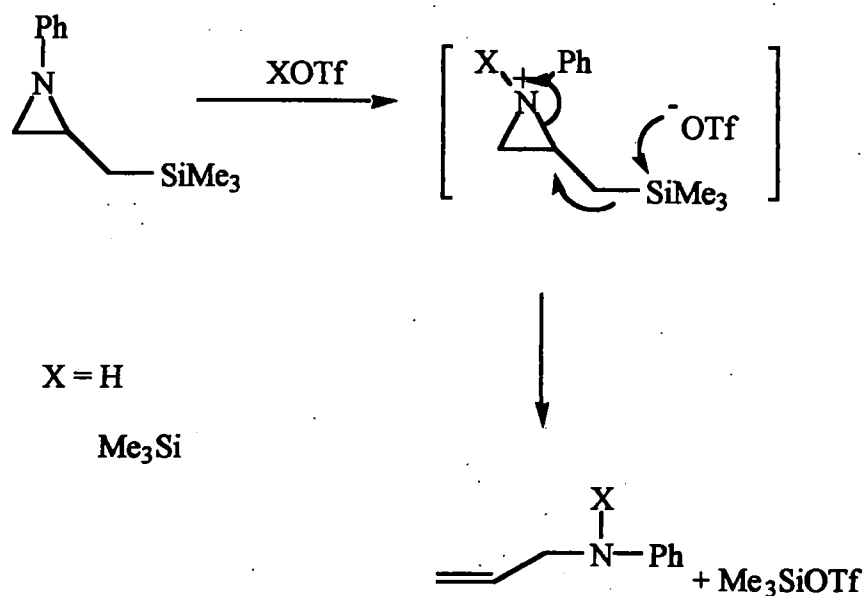
Trifluoromethanesulphonic acid, commonly known as triflic acid, is one of the strongest acids known, yet it is non-oxidising and stable to heat and water²⁸. Correspondingly the triflate anion is an extremely weak nucleophile. It was thought therefore that triflates would readily protonate, alkylate or silylate an aziridine on the nitrogen atom, possibly without ring destruction. Kyle performed a series of reactions with aziridines and triflates and obtained varying results, Scheme 4.45.



Scheme 4.45

The ring opening reaction of 1-carboethoxy-2-trimethylsilylaziridine with triflic acid to give the α ring opened product, most likely follows a similar mechanism to that for the ring opening with halogen acids. However, the enamine is most likely formed by an $\text{S}_{\text{N}}2$ mechanism involving an aziridinium salt, in which oxygen-silicon bond formation is simultaneous with, or precedes the carbon-nitrogen bond breaking.

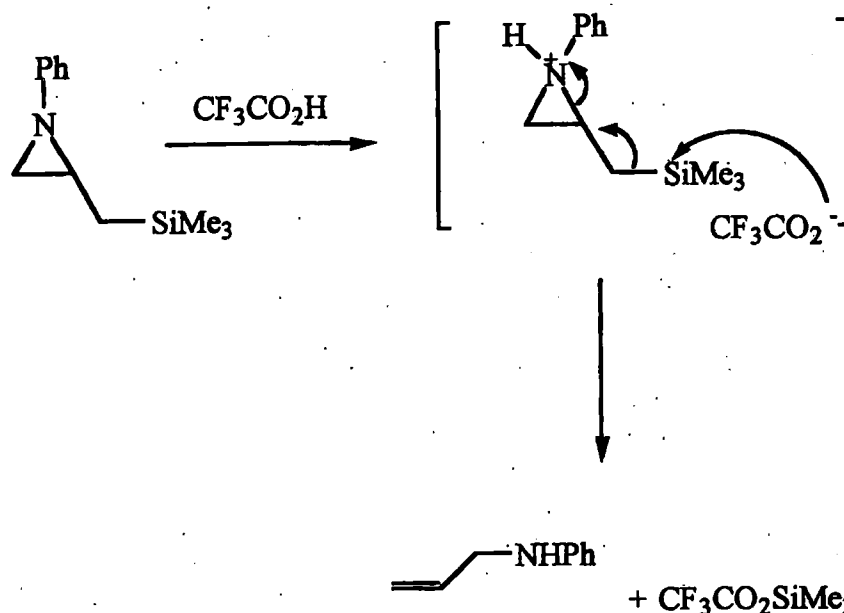
With β -trialkylsilylaziridines, all the triflates (HOTf , TMSOTf) reacted completely to give solely the allylamine, without any trace of β -addition product Scheme 4.46.



Scheme 4.46

4.5.7.3 Ring opening reaction with trifluoroacetic acid

In common with triflic acid, trifluoroacetic acid is a strong acid and provides an anion which is low in nucleophilicity. However, the anion is somewhat more basic than the triflate anion and probably more nucleophilic. Kyle observed that the reaction of trifluoroacetic acid with 2-trimethylsilylaziridines gave only the product of α - ring opening. In a previous study by Soobramanien, she was able to isolate a crystalline protonated trifluoacetate salt by reacting trifluoroacetic acid with *cis*-3-phenyl-1-propyl-2-trimethylsilylaziridine. With β -trialkylsilylaziridines, only the allylamine was formed, Scheme 4.47.

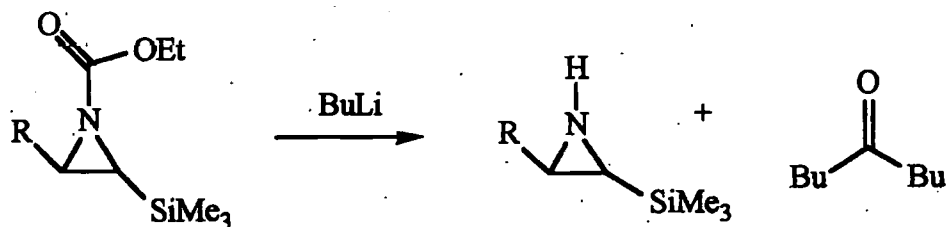


Scheme 4.47

4.5.8 Reactions of β -trialkylsilylaziridines with carbon nucleophiles (formation of a C-C bond).

The nucleophilic ring opening reactions of epoxides^{29,30} and aziridines^{31,32,33} with organometallic reagents have been studied as a convenient method for the generation of new carbon-carbon σ bonds. The utilisation of a Grignard reagent for the ring opening reactions of aziridines is a well established route, however, it has been limited in scope³⁴. The compatibility of cuprates with certain Lewis acids allows smooth ring-opening (complete regiocontrol-) of aziridines and epoxides under mild conditions. Scheme 4.48 below illustrates some of the reported reactions of organometallic reagents with aziridines and epoxides.

reacted 1-carboethoxy-2-trimethylsilylaziridine with n-butyllithium, the reaction occurred at the ester group, Scheme 4.49.



Scheme 4.49

We reacted a range of β -trialkylsilylaziridines with carbon nucleophiles, such as Grignard reagents, organocuprates, cyanide ion, carbanions from alkyl malonate and carbanions from acetylenes. In all cases, the reaction was not successful, resulting in recovery of starting materials or a mixture of unidentified products.

4.6 Summary of ring-opening reactions

N-phenyl- β -trialkylsilylaziridines undergo ring-opening reaction with various reagents in both acidic and non-acidic conditions, to give predominantly the product of β -attack, that is an " S_N1 "-type process. Substantial positive charge is formed on the β carbon which is stabilised by hyperconjugation with the Me_3SiCH_2 group. Phenol gave only the product of β attack, whereas thiophenol formed a mixture of two isomers, corresponding to β and γ - attack with β -attack predominating. Phenol is acidic enough to protonate the aziridine, whereas the thiophenol is less acidic and hence the positive charge build up in the transition state is not so great. With better nucleophiles such as azide and thiophenolate ion, it is not surprising that the " S_N2 "-type product starts to become more important. The implication

for the “S_N1”-type process, is that with the better nucleophile, there is less positive charge build up on the β-carbon so that hyperconjugation is less important in distinguishing between the two carbons.

There is growing evidence that γ-silyl carbonium ions can be stabilised³⁶. This stabilization is attributed to percaudal interactions in the w-conformation as illustrated in Figure 4.1.

This shows overlap of the reacting orbital on the α-carbon with the back lobe of the C-Si bonding orbital.

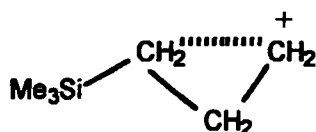


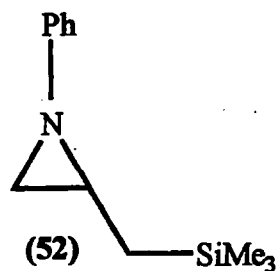
Figure 4.1

This is not possible in allylsilylaziridines because of the fixed geometry in the ring.

The oxygen nucleophiles, (MeO⁻, PhO⁻, ⁻OTf), fluorides and iodide, prefer to attack at the silicon. This is not surprising judging from the strong Si-X bond energies (where X = O, F, I).

A summary of the products formed from the reactions of the silyl aziridines with various nucleophilic reagents is given in Table 4.2.

of the type:



Reagent	Product	(%yield)
	(125)	70 ¹
NaN ₃	$\text{PhHNCH}_2 - \underset{\text{(126)}}{\underset{\text{N}_3}{\text{CH}}} \text{CH}_2\text{SiMe}_3 \quad 3 \quad : \quad \text{N}_3\text{CH}_2 - \underset{\text{(127)}}{\underset{\text{NHPH}}{\text{CH}}} \text{CH}_2\text{SiMe}_3 \quad 1$	58 ¹
PhSH or PhSNa	$\text{PhHNCH}_2 - \underset{\text{(128)}}{\underset{\text{SPh}}{\text{CH}}} \text{CH}_2\text{SiMe}_3 \quad 3 \quad : \quad \text{PhSCH}_2 - \underset{\text{(129)}}{\underset{\text{NHPH}}{\text{CH}}} \text{CH}_2\text{SiMe}_3 \quad 1$	80 ¹
PhOH	$\text{PhHNCH}_2 - \underset{\text{(130)}}{\underset{\text{OPh}}{\text{CH}}} \text{CH}_2\text{SiMe}_3 \quad \text{(130)}$	76 ¹
	$\text{PhHNCH}_2 - \underset{\text{(131)}}{\underset{\text{O-C}_6\text{H}_4\text{CH}_3}{\text{CH}}} \text{CH}_2\text{SiMe}_3 \quad \text{(131)}$	79 ¹
LiAlH ₄	$\text{PhHNCH}_2 - \text{CH}_2\text{CH}_2\text{SiMe}_3 \quad \text{(134)}$	52 ¹
MeO ⁻	$\text{CH}_2=\text{CHCH}_2\text{NHPH} \quad \text{(115)}$	-

1 = isolated product

4.7. Chapter Four References

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Experimental

5.1 Instruments and materials used

NMR spectra were recorded as solutions in deuteriochloroform with tetramethylsilane as internal standard on either JEOL FX 90Q or a JEOL EX 400 NMR spectrometer (*J* values are given in Hz).

Infrared spectra were obtained as Nujol mulls or thin films using sodium chloride plates or as KBr discs on a Nicolet 205 FT-IR spectrometer.

Mass spectra were run on a VG20-250 quadrupole instrument equipped with an Ion Tech fast atom bombardment (FAB) gun.

Butterworths and Medac Laboratories carried out elemental analyses.

Melting points were determined on a Buchi 510 melting point apparatus.

Weighings were done on a Sartorius 2000 MP digital balance.

Thin layer chromatography (TLC) was performed on a silica gel UV254 plates. Column chromatography was carried out using Merck Silica Kieselgel 60. Compounds were visualized using UV. light except were otherwise stated.

Where possible, elemental analyses or accurate masses have been reported. Work within the group over a number of years has shown that it is often very difficult to get accurate elemental analyses for some organosilicon compounds despite repeated submission of samples that have passed every other purity test. Hydrolysis and carbide formation lead to percentages that are consistently less than expected, thus although the majority of the elemental analyses quoted are acceptable, a few have one figure which falls short of ideal values. In all such cases, the experimental value is less than expected. Again, despite

repeated submissions we were unable to get any reasonable analyses on a small number of compounds and these are therefore not quoted. Accurate mass data is recorded where possible, however, this was limited since they were performed courtesy of Hoechst Roussel.

Materials used:

Tetrahydrofuran (THF) and diethylether were obtained from Aldrich Chemicals Co. Ltd. and were dried by distillation from sodium wire containing benzophenone and stored under an inert atmosphere prior to use.

Methanol, Ethanol, Toluene and Benzene (Aldrich Co. Ltd.) were used without distillation. Dichloromethane (Aldrich) was predried with calcium chloride and then distilled over calcium hydride before use.

Carbon tetrachloride (Aldrich) was stored over molecular sieve 4A and used without further distillation.

Hexane and Ethyl acetate (Aldrich Co. Ltd.) which were used for chromatography were not dried or distilled before use.

n Butyllithium, *sec*- Butyllithium and *t*- Butyllithium (Aldrich Co. Ltd) were stored below 0°C. N, N, N', N'-Tetramethylenediamine (Aldrich Chemical Co. Ltd.) was stored over molecular sieve 4A.

Copper (I) iodide (B. D. H. Chemical Co. Ltd.) was purified¹ before use.

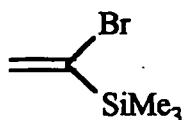
The trimethylsilyl halides and pseudohalides (Aldrich Chemical Co. Ltd.) were stored below 0°C.

Lithium aluminium hydride, boron trifluoride etherate, sodium borohydride, sodium cyanide, sodium azide, *p*-cresol, phenol (Aldrich Chemical Co. Ltd) were stored under nitrogen in a dessicator.

5.2. Preparation of starting materials.

5.2.1 Synthesis of vinyl-and allylsilanes

5.2.1.1 α -Bromovinyltrimethylsilane²



The preparation of this target silane occurred in two steps:

Step A: The preparation of α , β -dibromoethyltrimethylsilane

Step B: Dehydrobromination to give the bromosilane.

STEP A. Preparation of α , β -dibromoethyltrimethylsilane

In a three-necked round-bottom flask, immersed in a dry-ice/acetone bath was placed 100ml of dry dichloromethane and vinyltrimethylsilane (25.0g, 0.025mole). To this was added dropwise with stirring, dry liquid bromine (38.0g, 0.025mole). The bromine colour disappeared. Excess solvent was removed in vacuo to give 55.0g of nearly pure α , β -dibromoethyltrimethylsilane (b.pt 74-75°C, 8mmHg).

This step was repeated four times to give 220g of α , β -dibromoethyltrimethylsilane.

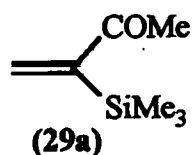
STEP B Preparation of α -Bromovinyltrimethylsilane

Diethylamine (121.0g, 1.66mole) dried over sodium hydroxide, was shaken in a flask with α , β -dibromoethyltrimethylsilane, (217g, 0.83mole) at room temperature for 20hrs.

The precipitate of diethylamine hydrobromide was filtered off and washed several times with ether.

The filtrate was washed with 5% cold hydrochloric acid several times to remove excess diethylamine, followed by water and dried over anhydrous magnesium sulphate. The solvent was removed by distillation and the bromosilane collected at 26-27°C 15mmHg (lit² b.pt. 32°C 17mmHg), yield 135g (91%): ¹H NMR (400 MHz, CDCl₃) δ 0.80 (s, 9H), 6.60-6.80 (m, 2H); ¹³C NMR (400 MHz, CDCl₃) δ 0.01 (SiMe₃), 131 (CH₂=C), 141 (CH₂=CBr).

5.2.1.2 3-Trimethylsilylbut-3-en-2-one (29a)³.



The 3-Trimethylsilylbut-3-en-2-one was synthesised in two steps via the synthesis of 4-trimethylsilylbut-3-en-2-ol and its subsequent oxidation using Jones reagent to give the ketone.

STEP A: Synthesis of 4-trimethylsilylbut-3-en-2-ol

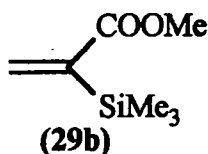
A solution of α-bromovinyltrimethylsilane (3.04g, 0.017mole) in dry THF (50ml) was cooled to -110°C with stirring under a nitrogen atmosphere. *tert*-Butyllithium in pentane (11.2 ml, 0.019mole) was added dropwise over 10mins, maintaining the temperature below -100°C throughout. The bright yellow solution was stirred for a further 30mins. at -100°C. Freshly distilled acetaldehyde (0.035mole) was added dropwise to the solution, which turned colourless. After 1.5hrs, the mixture was worked up at room temperature by pouring in pre-cold aq. sat. ammonium chloride solution and the organic layer extracted using

diethylether and dried with anhydrous magnesium sulphate. Removal of solvent using rotatory evaporator gave the alcohol 4-trimethylsilylbut-3-en-2-ol in high yield (83%, 2.4g):

^1H NMR (400 MHz, CDCl_3) δ 0.12 (s, 9H, SiMe_3), 1.28 (d, $J=6.4$ Hz, 3H, CH_3), 4.46 (q, $J=6.4$ Hz, 1H, CH), 5.35-5.70 (dd, $J=2.4, 2.4$ Hz, 2H, $\text{CH}_2=\text{C}$); ^{13}C NMR (400 MHz, CDCl_3) δ 0.013 (SiMe_3), 24.75 (CH_3), 72.43 (CH), 123.36 (CSiMe_3), 157.3 ($\text{CH}_2=\text{C}$); ^{29}Si NMR (400 MHz, CDCl_3) δ -4.7. It was used in the next stage without further purification.

STEP B: Oxidation of 4-trimethylsilylbut-3-en-2-ol

A slurry of pyridinium chlorochromate (PCC), (12.93g, 0.06mole) in 50ml of dry dichloromethane was stirred at room-temperature for 15mins. To this was added 4-trimethylsilylbut-3-en-2-ol, (2.89g, 0.02mole) in 5ml dichloromethane and the mixture was stirred for a further 1.5hrs. The solution was decanted from the solid mixture and washed with 200ml of diethylether. The solution was washed further with 5% aq. sodium hydroxide, 100ml, 5% hydrochloric acid, 100ml, 5% sodium bicarbonate and 100ml of saturated sodium chloride solution. The organic layer was then dried with powdered anhydrous magnesium sulphate. Removal of the solvent and purification by distillation gave a sweet smelling liquid 1.2g (40%) yield : ^1H NMR (400 MHz, CDCl_3) δ 0.14 (s, 9H, SiMe_3), 2.29 (s, 3H, CH_3CO), 6.17 and 6.50 (d, 1H, $J=1.6\text{Hz}$ and d, 1H, $J=2.0\text{Hz}$, $\text{CH}_2=\text{C}$) ^{13}C NMR (400MHz, CDCl_3) δ -0.12 (SiMe_3) 26.95 (COCH_3), 137.50 ($\text{CH}_2=\text{C}$), 154.76 ($\text{CH}_2=\text{C}$), 205 (CO). ^{29}Si NMR (400 MHz, CDCl_3) δ 0.00.



STEP A:

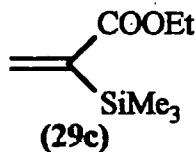
Trimethylsilylacrylic acid

A solution of α -bromovinyltrimethylsilane, (3.04g, 0.017mole) in dry THF (50ml) was cooled to -100°C with stirring under a nitrogen atmosphere. *tert*-Butyllithium in pentane, (11.2ml, 0.019mole) was added dropwise over 10mins. maintaining the temperature at -110°C throughout. The bright yellow solution was stirred for a further 30 mins at -100°C . This solution was then slowly poured onto a rapidly stirred slush of solid carbon-dioxide (excess) in ether. After all the carbon dioxide had disappeared, the solution was hydrolysed by pouring into a beaker containing finely crushed ice-water with a little conc.HCl. The organic layer was extracted with ether, washed with water several times, followed by sodium bicarbonate solution. After drying with anhydrous magnesium sulphate, the solvent was removed to afford trimethylsilylacrylic acid, 1.5g (60%) yield.

^1H NMR (400 MHz, CDCl_3) δ 0.19 (s, 9H, SiMe_3), 6.12 and 6.89 (d, 1H, $J=2.4$ Hz and d, 1H, $J=3.2$ Hz, $\text{CH}_2=\text{C}$); 11.24 (s, 1H, OH); ^{13}C NMR (400 MHz, CDCl_3) δ -0.86 (SiMe_3), 142.09 (CH_2), 148.47 (CSi), 175.76 (CO). ^{29}Si NMR (400 MHz, CDCl_3) δ -2.88. It was used in the next step without further purification.

STEP B:**Esterification of trimethylsilylacrylic acid**

To trimethylsilylacrylic acid (16.1g, 0.11mole) in methanol (35ml) was added conc. sulphuric acid (0.9ml) and the mixture refluxed for 15hrs. The mixture was hydrolysed with water and the organic layer extracted with ether, washed several times with water and then with sodium bicarbonate solution. The organic layer was dried using anhydrous magnesium sulphate. Removal of solvent in vacuo and purification by column chromatography using hexane / ethylacetate as the eluent afforded methyl 2-(trimethylsilyl)acrylate, 14.0g (80%): ^1H NMR (400 MHz, CDCl_3) δ 0.15 (s, 9H, SiMe_3), 3.7 (s, 3H, OMe), 5.9 and 6.7 (d, 1H, $J=2.8$ and d, 1H, $J=2.8$, $\text{CH}_2=\text{C}$); ^{13}C NMR (400MHz, CDCl_3) δ -0.85 (SiMe_3), 52.15 (OCH_3), 139.92 ($\text{CH}_2=\text{C}$), 144.78 ($\text{CH}_2=\text{C}$), 170.40 (CO). ^{29}Si NMR (400 MHz, CDCl_3) δ -3.16.

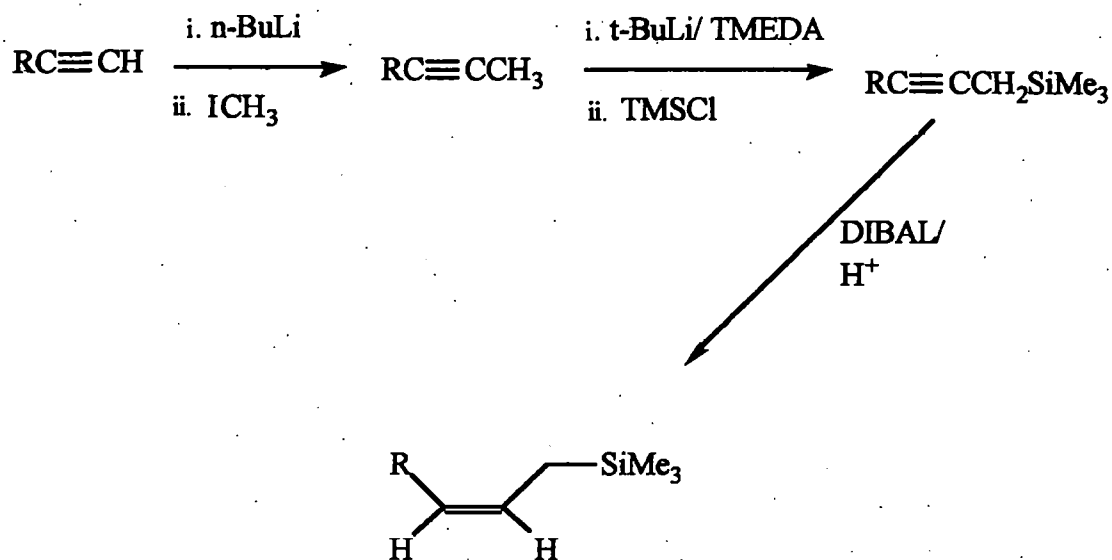
5.2.1.4.**Ethyl 2-(Trimethylsilyl)acrylate(29c)²**

To trimethylsilylacrylic acid (16.1g, 0.11mole) (prepared as described above) in ethanol (35ml) was added conc. sulphuric acid (0.9ml) and the mixture refluxed for 15hrs. The mixture was hydrolysed with water and the organic layer extracted with ether, washed several times with water and then with sodium bicarbonate solution and the procedure for the isolation and purification was similar to that described in section 7.2.1.3. The yield of the isolated ethyl 2-(trimethylsilyl)acrylate was 16.5g (85%).:

^1H NMR (400 MHz, CDCl_3) δ 0.16 (s, 9, SiMe_3), 1.29 (t, $J=7.4$ Hz, 3H, CH_3), 4.18 (q, $J=7.32$ Hz, 2H, CH_2), 5.98 and 6.77 (d, $J=2.8$ Hz, 1H and d, $J=2.8$ Hz, 1H, $\text{CH}_2=\text{C}$); ^{13}C NMR (400 MHz, CDCl_3) δ -0.76 (SiMe_3), 14.73 (CH_3), 61.00 (OCH_2), 139.71 ($\text{CH}_2=\text{C}$), 145.07 ($\text{CH}_2=\text{C}$), 169.96 (CO). ^{29}Si NMR (400 MHz, CDCl_3) δ -3.30.

5.2.1.5 Synthesis of *cis*-allylsilanes

The general scheme for the synthesis of this class of silanes is shown below:



General procedure for preparation of 2-alkyne

To 1-alkyne (0.10mol) in dry THF in (50ml) in an oven-dried three-necked flask under nitrogen at 0°C was added dropwise by a gas tight syringe *n*-BuLi (0.11mole, 59.4ml of 2.5M). The reaction mixture was refluxed for 20 min, and then cooled to room temperature. To this was added dropwise iodomethane (0.11mol, 15.6g, 6.85ml) dissolved in THF (10ml) over a 20min. period. The reaction mixture was then stirred at room temperature for 3hrs. and then hydrolysed with water. The organic layer was extracted with ether and dried using MgSO_4 .

Removal of excess solvent by rotatory evaporator and purification by simple distillation gave the 2-alkyne.

The following 2-alkynes silanes and their subsequent conversion to propargylsilanes are all known and hence no further characterisation was done as the NMR data corresponded to that of literature.

Preparation of 2-heptyne⁴

See the general procedure: 1-hexyne (11.09g, 0.135 mol.) was used. The yield of the 2-heptyne was 8.5g, (65%). ν_{\max} (neat film/cm⁻¹) 2959.0 (s, CH), 2932.0 (s, CH₃), 2873.5 (m, CH₃), 2862.6 (m, CH₂), 2053.0 (vw, CC), 1466.0 (m, CH), 1458.0 (m, CH); ¹H NMR (400 MHz, CDCl₃) 0.88 (3H, t, CH₃), 1.47-1.32 (4H, m, CH₂), 1.75 (3H, t, CH₃-CC), 2.12-2.07 (2H, m, CH₂-CC); ¹³C NMR (400 MHz, CDCl₃) 3.85 (1C, CH₃-CC), 14.06 (1C, CH₃), 18.87 (1C, CH₂), 22.42 (1C, CH₂), 31.67 (1C, CH₂), 75.71 (1C, t, -C-Me), 79.77 (1C, t-C-C₄).

Preparation of 2-nonyne⁴

See the general procedure: 1-octyne (14.88g, 0.135 mol). The yield of product was 14.5g (87%). ν_{\max} (neat film/cm⁻¹) 2958.0 (s, CH), 2931.0 (s, CH₃), 2872.0 (s, CH₃), 2859.3 (s, CH₂), 2052.7 (vw, CC), 1466.7 (m, CH), 1458.7 (m, CH₂); ¹H NMR (400 MHz, CDCl₃) 0.856 (3H, t, J=5.7 Hz, CH₃-CH₂), 1.73 (3H, t, J=2.5 Hz, CH₃-C), 2.03-2.09 (2H, m, CH₂-C); ¹³C NMR (400 MHz, CDCl₃) 3.84 (1C, CH₃-C), 14.52 (1C, CH₃-CH₂), 19.29 (1C, CH₂), 21.93 (1C, CH₂), 23.14 (1C, CH₂), 29.17 (1C, CH₂), 31.99 (1C, CH₂-C), 75.70 (1C, C-CH₃), 79.84 (1C, C-CH₂).

General procedure for preparation of propargylsilanes

To a solution of *t*-BuLi (0.1mole, 61.8 ml, 1.7 M in pentane), cooled to -78°C, was added sequentially with stirring THF (100 ml), TMEDA (0.1mol, 11.6g, 15ml) and the 2-alkyne (0.1mol) under nitrogen. The yellow slurry thus produced was allowed to come to 0°C, and was stirred at this temperature for a further hour. The yellow solution was then cooled to -78°C, and treated dropwise with TMSCl (0.12mol, 13g, 15.2ml). The mixture, on reaching ambient temperature, was poured on to ice-water (100 ml), and the layers were separated. The aqueous layer was extracted with ether (3x100 ml), and the combined extracts were washed with aqueous HCl (100ml, 3M), brine and dried with anhydrous MgSO₄. Removal of the solvent by rotary evaporator and purification by simple distillation gave the product.

Preparation of 1-trimethylsilyl-2-heptyne⁴

Using 2-heptyne (9.6g, 0.1mol) as described in the procedure above, the yield of the product was 13.0g, (77%). ν_{\max} (neat film/cm⁻¹) 2957.6 (s, CH), 2933.3 (m, CH₃), 2875.6 (w, CH₃), 2863.9 (w, CH₂), 2222.0 (very weak, CC), 1466.8 (w, CH), 1458.9 (w, CH₂), 1249.0 (s, SiMe) and 850.6 (s, CH); ¹H NMR (400 MHz, CDCl₃) 0.08 (9H, s, SiMe₃), 0.89 (3H, t, J=7.4 Hz, CH₃), 1.37-1.47 (6H, m, CH₂), 1.41 (2H, t, J=2.7 Hz, CH₂-Si), 2.11-2.15 (2H, m, CH₂); ¹³C NMR (400 MHz, CDCl₃) -1.63 (3C, SiMe₃), 7.40 (1C, CH₂Si), 1410 (1C, CH₃), 19.07 (1C, CH₂), 22.40 (1C, CH₂), 32.04 (1C, CH₂), 77.72 (1C, t-C-CH₂Si) and 79.38 (1C, t-C).

Preparation of 1-trimethylsilyl-2-nonyne⁴

See the general procedure. 2-nonyne (12.42g, 0.1mol). The yield of the product was 16.5g, (84%). ν_{\max} (neat film/cm⁻¹) 2957.0 (s, CH), 2931.0 (s, CH₂), 2874.4 (s, CH₃), 2859.1 (s, CH₂), 2222.3 (very weak, CC), 1467.0 (w, CH), 1458.9 (w, CH₂), 1249.2 (s, SiMe), 851.3 (s, CH); ¹H NMR (400 MHz, CDCl₃) 0.08 (9H, s, SiMe₃), 0.89 (3H, t, J=8.6 Hz, CH₃), 1.41 (2H, t, J=2.7 Hz, CH₂-Si), 1.24-1.47 (8H, m, CH₂), 2.15-2.10 (2H, m, CH₂-C), ¹³C NMR (400 MHz, CDCl₃) -2.13 (3C, SiMe₃), 6.90 (1C, CH₂-Si), 14.03 (1C, CH₃), 18.90 (1C, CH₂), 22.61 (1C, CH₂), 28.54 (1C, CH₂), 29.42 (1C, CH₂), 31.41 (1C, CH₂-C), 77.24 (1C, C-CH₂Si), 78.94 (1C, C-CH₂).

Preparation of 1-trimethylsilyl-2-hexyne⁴

Repeating the reaction with 2-hexyne (8.2g, 0.1mol, 11.2ml) from Aldrich. The yield of the product was 11.5g (75%). ¹H NMR (400 MHz, CDCl₃) -0.08 (9H, s, SiMe₃), 0.96 (3H, t, J=7.3 Hz), 1.41 (2H, t, J=2.7 Hz, CH₂Si), 1.46-1.51 (2H, m, CH₂-Me), 2.14-2.09 (2H, m, CH₂-C), ¹³C NMR (400 MHz, CDCl₃) -1.41 (3C, SiMe₃), 7.60 (1C, CH₂-Si), 14.17 (1C, CH₃), 21.65 (1C, CH₂-Me), 23.51 (1C, CH₂-C), 78.12 (1C, CH-CH₂Si), 79.47 (1C, CH-CH₂).

General procedure for the reduction of propargylsilanes to *cis* allylsilanes:

To a solution of 1-trimethylsilyl-2-alkyne (0.02mol) in hexane (20ml) was added neat DIBAL (0.04mol, 7.1ml) using a syringe, and the reaction temperature maintained at 25-30°C by means of a water bath. The solution was stirred at ambient temperature for 30 min. and then heated at 70°C for 4hrs. On cooling to ambient temperature, the reaction mixture was transferred using a double-ended needle to a vigorously stirred mixture of aqueous HCl (120ml, 3M), ice (120g) and pentane (60ml). The mixture was stirred for a further 15min, the layers separated, and the aqueous layer extracted with pentane (3x60ml). The combined organic extracts were washed with water (100ml) and brine (100ml), and dried. Removal of the solvent in vacuo and purification by simple distillation gave the product.

This stereoselective synthesis of *cis*-allylsilanes from propargylsilanes has been reported and hence no further characterisation of the alkenes was done, as the NMR data was in agreement with the literature^{5,6}.

Preparation of *cis*-1-trimethylsilyl-2-heptene⁶

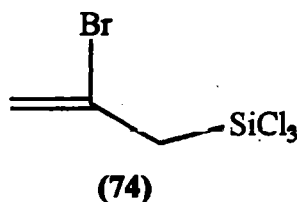
Using mole of 1-trimethylsilyl-2-heptyne (3.3g, 0.02mol), the yield of the *cis*-alkene was 2.70g (81%) yield. ν_{\max} (neat film/cm⁻¹) 3007.4 (m), 2957.0 (s, CH), 2927.8 (s, CH₃), 2874.4 (m, CH₃), 2860.8 (m, CH₂), 1466.6(w, CH), 1458.6 (w, CH₂), 1248.7 (s, SiMe), 1151.3 (m,), 854.8 (vs, CH), 840.9 (vs, CH), 725.9 (m), 699.7 (m); ¹H NMR (400 MHz, CDCl₃) 0.04 (9H, s, SiMe₃), 0.90 (3H, t, J=6.4 Hz, CH₃), 1.30-1.36 (4H, m, CH₂), 1.47 (2H, d, J=8.3 Hz, CH₂-Si), 1.99 (2H, m, CH₂), 5.23-5.35 (1H, m, CH-CH₂-Si), 5.34-5.43 (1H, m, CH), ¹³C NMR (400 MHz, CDCl₃) -1.29 (3C, SiMe₃), 14.55 (1C, CH₃), 18.89 (1C, CH₂-Si), 23.00 (1C, CH₂), 27.28 (1C, CH₂), 32.55 (1C, CH₂), 125.71 (1C, CH-C-Si), 128.23 (1C, CH).

Preparation of *cis*-1-trimethylsilyl-2-nonene⁶

When 1-trimethylsilyl-2-nonyne (11.78g, 0.60mol) was used as described above, the yield of the product was 16.5g (76%). ν_{\max} (neat film/cm⁻¹) 3006.9 (m), 2956.0 (s, CH), 2926.0 (s, CH₃), 2873.4 (m, CH₃), 2856.6 (m, CH₂), 1645.3 (vw, C=C), 1467.0 (w, CH), 1459.5 (w, CH₂), 1248.5 (s, SiMe), 1151.9 (m,), 854.7 (vs, CH), 720.2 (w), 701.5 (w), 662.4 (w); ¹H NMR (400 MHz, CDCl₃) 0.01(9H, s, SiMe₃), 0.89 (3H, t, J 6.3 Hz, CH₃), 5.42-5.34 (1H, m, CH), 1.23-1.35 (8H, m, CH₂), 1.46 (2H, d, J=8.3Hz, CH₂-Si), 1.95-2.00 (2H, m, CH₂-CH), 5.31-5.23 (1H, m, CH-CH₂-Si), ¹³C NMR (400 MHz, CDCl₃) -1.09 (3C, SiMe₃), 14.81 (1C, CH₃), 19.11 (1C, CH₂-Si), 23.38 (1C, CH₂), 27.79 (1C, CH₂), 29.86 (1C, CH₂), 30.52 (1C, CH₂), 32.55 (1C, CH₂-CH), 125.89 (1C, CH-CH₂-Si), 128.50 (1C, CH).

Preparation of *cis*-1-trimethylsilyl-2-hexene⁶

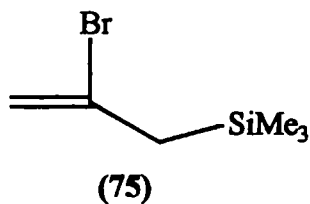
Using of 1-trimethylsilyl-2-hexyne, (3.1g, 0.02mol), the yield of the product was 2.65g (84%). ¹H NMR (400 MHz, CDCl₃) 0.00 (9H, s, SiMe₃), 0.90 (3H, t, J=7.3 Hz, CH₃), 1.32-1.41 (2H, m, CH₂-Me), 1.47 (2H, d, J=8.8 Hz, CH₂-Si), 1.93-1.99 (2H, m, CH₂-CH), 5.24-5.30 (1H, m, CH-CH₂-Si), 5.43-5.36 (1H, m, CH), ¹³C NMR (400 MHz, CDCl₃) -1.09 (3C, SiMe₃), 14.62 (1C, CH₃), 19.11 (1C, CH₂Si), 23.64 (1C, CH₂-Me), 29.86 (1C, CH₂-CH), 126.09 (1C, CH-CH₂-Si), 128.23 (1C, CH).



A mixture of trichlorosilane (18.9g, 0.14mole) and 2,3-dibromoprop-1-ene, (25g, 0.12mole) was added dropwise, under a nitrogen atmosphere, to a stirred mixture of triethylamine (16ml, 0.12mole), cuprous chloride (0.008mole) and dry ether (100ml). Stirring was continued at room temperature for a further 4hrs. The mixture was filtered and the filtrate concentrated to give 25.6g (92%) of 2-bromo-3-trichlorosilyl-propene, 74.

¹H NMR (400 MHz, CDCl₃) δ 2.24 (s, 2H, SiCH₂), 5.6-5.9 (m, 2H, =CH₂). This was used in the next step without any further purification.

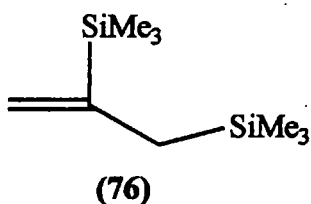
The Grignard reagent from 74, was generated in ether using magnesium turnings (8.4g, 0.35 mole) and methyl iodide (46.8g, 0.33mole). To this was added, dropwise at 0°C, 2-bromo-2-trichlorosilylpropene (28.0g, 0.11mole), and the reaction allowed to warm up to room temperature and stirring continued for 10hrs. The reaction mixture was then hydrolysed with aqueous ammonium chloride solution and the organic layer extracted with ether. Removal of the solvent in vacuo gave a pale yellow oil which was purified by chromatography over silica gel using hexane/dichloromethane as the eluent to give 12g (56%) of 2-bromo-3-trimethylsilyl propene 75 as a colourless oil.



ν_{max} (neat film/ cm^{-1}) 2960, 2900, 1620, 1410, 1250, 1195, 1160, 1080, 930, 805, 690; ^1H NMR (400 MHz, CDCl_3) δ 0.00(s, 9H, SiMe_3), 1.98 (s, 2H, SiCH_2), 5.09 (bs, 1H, $=\text{CH}_2$), 5.19 (bs, 1H, $=\text{CH}_2$); ^{13}C NMR (400 MHz, CDCl_3) δ -0.26 (SiMe_3), 34.63(CH_2Si), 115.18 ($=\text{CBr}$), 132.42 ($=\text{CH}_2$).

5.2.1.8 2,3-Bis(trimethylsilyl)propene (76)⁷

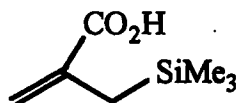
A solution of 2-bromo-3-trimethylsilylpropene (12.6g, 0.065 mole) in dry THF (50ml) was cooled to -110°C with stirring under nitrogen. *tert*-Butyllithium in pentane (11.2ml, 0.019mole) was added dropwise over 10mins. maintaining the temp. below -100°C throughout. The bright yellow solution was stirred for a further 30mins at -100°C . Chlorotrimethylsilane (10.71g, 0.065mole) was added dropwise with the temperature maintained at -100°C for a further 20 mins. The mixture was then allowed to warm slowly to room temperature and stirred for an additional 17hrs. Hydrolysis at 0°C with saturated ammonium chloride solution was followed by extraction with ether and dried using MgSO_4 . The product was purified by column chromatography to give 2,3-bis (trimethylsilyl)propene, 76 as a colourless oil 6.5g (54%).



^1H NMR (400 MHz, CDCl_3) δ 0.07 (s, 9H, SiMe_3), 0.12 (s, 9H, SiMe_3), 1.69 (bs, 2H, CH_2Si), 5.28 (d, 1H, $J=2.8\text{Hz}$, $\text{CH}_2=$), 5.48 (d, 1H, $J=2.8\text{Hz}$, $\text{CH}_2=$); ^{13}C NMR (400 MHz, CDCl_3) δ -1.45 (SiMe_3), -1.25 (SiMe_3), 22.50 (CH_2Si), 122.95 ($\text{CH}_2=$), 149.31(CSi); MS (EI+) m/e 187(1.4), 179(5), 171(8), 165(2), 163(5), 155(6), 147(26), 123(14), 73(100), 59(10), 57(26), 45(22), 43(10), 41(11), 29(4.7).

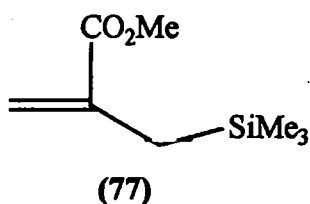
5.2.1.9 2-Carbomethoxy-3-trimethylsilylpropene (77)⁸

A solution of 2-bromo-3-trimethylsilylpropene, (3.2g, 0.017mole) in dry THF (50ml) was cooled to -100°C with stirring under a nitrogen atmosphere. *tert*-butyllithium in pentane, (11.2ml, 0.019mole) was added dropwise over 10mins maintaining the temperature at -110°C throughout. The bright yellow solution was stirred for a further 30mins. at -100°C . This solution was then slowly poured onto a rapidly stirred slush of solid carbon dioxide (excess) with ether in a beaker. After all the carbon dioxide had disappeared, the solution was then hydrolysed by pouring into a beaker containing finely crushed ice-water with a small amount of conc. HCl. The organic layer was extracted with ether, washed with water several times, followed by sodium bicarbonate solution and dried with anhydrous MgSO_4 . Removal of the solvent afforded the 3-trimethylsilyl acrylic acid 1.0g (37%) which was used without further purification.



^1H NMR (60MHz) δ 0.45 (s, 9H, SiMe_3), 2.35 (s, 2H, SiCH_2), 2.50 (bs, 1H, OH-600Hz offset), 5.82 and 6.66 (dd, 2H, CH_2).

To 3-trimethylsilylacrylic acid (1.0g, 0.006mole) in ethanol (15ml) was added conc.sulphuric acid (0.9ml) and the mixture refluxed for 15hrs. The mixture was hydrolysed with water and the organic layer extracted with ether, washed several times with water followed by sodium bicarbonate solution and dried over anhydrous MgSO_4 . Removal of solvent in vacuo and purification by column chromatography using hexane/dichloromethane as the eluent afforded 0.6g (55%) of 2-carbomethoxy-3-trimethylsilylpropene 77.



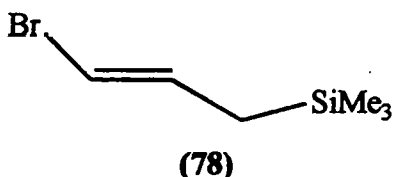
ν_{max} (neat film/ cm^{-1}) 2954, 1723, 1650, 1475, 1325, 1303, 1249, 1197, 1175, 1103, 856;
 ^1H NMR (400 MHz, CDCl_3) δ 0.00 (s, 9H, SiMe_3), 1.83(bs, 2H, CH_2Si), 3.73 (s, 3H, OMe), 5.31(s, 1H, $\text{CH}_2=$), 5.98 (s, 1H, $\text{CH}_2=$); ^{13}C NMR (400 MHz, CDCl_3) δ - 1.68 (SiMe_3), 22.40 (CH_2Si), 51.92 (OCH_3), 121.87 ($\text{CH}_2=$), 138.47($=\text{C}$), 168.28 (CO); MS (EI+) m/e 157(- CH_3 (11)), 1323(5), 119(6), 105(8), 95(12), 89(19), 79(9), 73518), 73(100), 68(12), 59(12), 57(16), 45(11), 43(13), 41(13); Analysis cal'd for $\text{C}_8\text{H}_{16}\text{SiO}_2$: C 55.7 H 9.3; Found C 55.3 H 9.3.

5.2.1.10 1-Bromo-3-trimethylsilylpropene (78)⁹

Tol-bromopropene (24.2g, 0.2mole) in a 250ml round bottom flask containing 100ml carbon tetrachloride was added N-bromosuccinimide (NBS), (36.0g, 0.2mole) with stirring. To this mixture was added benzoyl peroxide (0.24g, 1mole). The mixture was then refluxed for 1.5hrs. The mixture was cooled, filtered and the solution, concentrated using a rotary evaporator to give 1,3-dibromopropene 19.2g, (50%) as an oil, which was used in the next step without further purification.

A mixture of trichlorosilane (16.25g, 0.12mole) and 1,3-dibromoprop-1-ene (19.2g, 0.10mole) was added dropwise, under a nitrogen atmosphere, into a stirred mixture of triethylamine (16ml, 0.12mole), cuprous chloride (0.008mole) and dry ether (100ml). Stirring was continued at room temperature for a further 4hrs. The mixture was filtered and the filtrate concentrated in vacuo to give 1-bromo-3-trichlorosilylpropene, 18.0g (77%). This was used in the next step without any further purification.

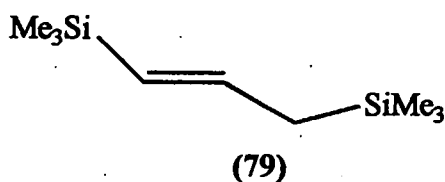
A Grignard reagent of 3-bromo-2-trichlorosilylpropene was generated in ether magnesium turnings from (5.28g, 0.22mole) and methyl iodide (30.11g, 0.21 mole). To this was added dropwise at 0°C, 1-bromo-3-trichlorosilylpropene (18.0g, 0.07mole), and the reaction allowed to warm up to room temperature and stirring continued for 10hrs. The reaction mixture was then hydrolysed with aqueous ammonium chloride solution and the organic layer extracted with ether. Removal of the solvent in vacuo gave a pale yellow oil which was purified by chromatography over silica gel using hexane/dichloromethane as the eluent to give 12g (88%) of 1-bromo-3-trimethylsilyl propene 78 as a colourless oil.



^1H NMR (400 MHz, CDCl_3) δ 0.08(s, 9H, SiMe_3), 1.47 (d, 2H, $J=8.8\text{Hz}$, CH_2Si), 6.12 (m, 2H, $\text{CH}=\text{CH}-$); ^{13}C NMR (400 MHz, CDCl_3) δ 0.00 (SiMe_3), 22.84 (CH_2Si), 106.72($=\text{CH}$), 131.87($\text{CH}=\text{}$).

5.2.1.11 1,3-Bis(trimethylsilyl)propene (79)¹⁰

A solution of 1-bromo-3-trimethylsilylpropene (12.6g, 0.065 mole) in dry THF (50ml) was cooled to -110°C with stirring under nitrogen. *tert*-Butyllithium in pentane (11.2ml, 0.019mole) was added dropwise over 10mins. maintaining the temp. below -100°C throughout. The bright yellow solution was stirred for a further 30mins at -100°C . Chlorotrimethylsilane 10.71g (0.065mole) was added dropwise and the temperature maintained at -100°C for a further 20mins. The mixture was then allowed to warm slowly to room temperature and stirred for an additional 17 hrs. Hydrolysis at 0°C with saturated ammonium chloride solution was followed by extraction with ether and the organic layer dried using MgSO_4 . The product was purified by column chromatography to give 1,3-bis(trimethylsilyl)propene 7.0g (57%).

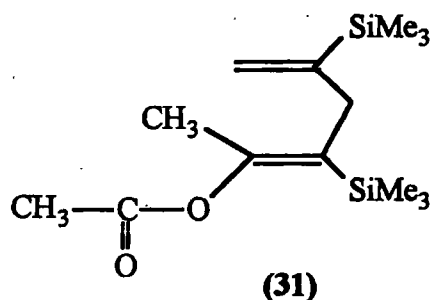


^1H NMR (400 MHz, CDCl_3) δ 0.00 (s, 9H, SiMe_3), 0.08 (s, 9H, SiMe_3), 1.5 [m, 4H, 2 (CH_2Si)], 5.3 (m, 2H, $-\text{CH}=\text{CH}-$); ^{13}C NMR (400 MHz, CDCl_3) δ -0.47(SiMe_3), -0.26 (SiMe_3), 19.26 (CH_2Si), 24.23 (CH_2Si), 124.37($\text{CH}=\text{}$), 125.76($\text{CH}=\text{}$).

5.3 Reactions of α -lithiovinyltrimethylsilane with carbonyl compounds.

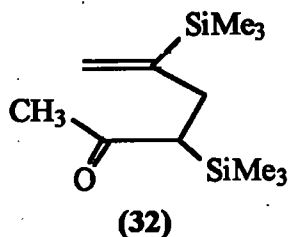
5.3.1 3,5-bis(trimethylsilyl)hexa-2,5-dien-2-yl acetate(31)

A solution of α -bromovinyltrimethylsilane (3.04g, 0.017mole) in dry THF (50ml) was cooled to -110°C with stirring under nitrogen. *tert*-Butyllithium in pentane (11.2ml, 0.019mole) was added dropwise over 10 mins., maintaining the temperature below -100°C throughout. The bright yellow solution was stirred for a further 30mins at -100°C . Acetic anhydride (0.025mole) was added dropwise over 10mins and the temperature maintained at -100°C for a further 20mins. The mixture was then allowed to warm slowly to room temperature and stirred for an additional 17hrs. Hydrolysis at 0°C with saturated ammonium chloride solution was followed by extraction with ether. The organic layer was dried using anhydrous MgSO_4 . After removal of solvent using a rotary evaporator, the crude product was purified by column chromatography using silica gel with hexane as the eluent to give 3,5-bis(trimethylsilyl)hexa-2,5-dien-2-yl acetate 31, 4.10g (85%). Reacting the anion with acetyl chloride gave the same product in 65% yield.



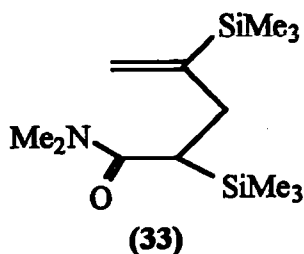
^1H NMR (400 MHz, CDCl_3) δ 0.07 (s, 9H, SiMe_3), 0.12 (s, 9H, SiMe_3), 2.03 (s, 3H, CH_3), 2.05 (s, 3H, CH_3CO -), 2.78 (s, 2H, $\text{C}=\text{C}-\text{CH}_2-\text{C}=\text{C}$), 5.42-5.47 (m, 2H, $\text{CH}_2=\text{C}$); ^{13}C NMR (400 MHz, CDCl_3) δ -1.23, 0.26 (2x SiMe_3), 20.58 (CH_3), 21.40 (CH_3CO), 34.33 (CH_2), 121.07 (CCH_3), 123.75 ($\text{CH}_2=\text{C}$), 149.95 (CSi), 152.15 (CSi), 169.54 (CO); ^{29}Si NMR (400 MHz, CDCl_3) δ -3.65, -3.30; Analysis calc'd for $\text{C}_{14}\text{H}_{28}\text{Si}_2\text{O}_2$: Calcd. C 59.1 H 9.9; Found C 58.9 H 9.7.

5.3.2 3,5-bis(trimethylsilyl)hex-5-en-2-one (32)



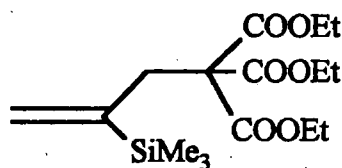
When the procedure described in 5.3.1 was carried out using ethyl acetate as the acylating agent, 3,5-bis(trimethylsilyl)hex-5-en-2-one 32 was obtained: ^1H NMR (400 MHz, CDCl_3) δ 0.10 (s, 9H, SiMe_3), 0.11 (s, 9H, SiMe_3), 2.04 (s, 3H, COCH_3), 2.19 (m, 1H, $\text{CH}_2=\text{C}-\text{CH}_2-\text{CHSi}$), 2.67-2.75 (m, 2H, $\text{CH}_2=\text{C}-\text{CH}_2\text{CH}$), 5.27-5.46 (m, 2H, $\text{CH}_2=\text{C}$); ^{13}C NMR (400 MHz, CDCl_3) δ -1.51, -2.46 (2x SiMe_3), 31.57 (CH_3), 32.63 (CH_2), 47.63 (CHSi), 123.67 ($\text{CH}_2=\text{C}$), 151.40 ($\text{C}=\text{CSi}$), 209.33 (CO).

5.3.3 1-Dimethylamido-1,3-bis(trimethylsilyl)but-3-ene (33)



1-Dimethylamido-1,3-bis(trimethylsilyl)but-3-ene was isolated from the product mixture when dimethyl carbamyl chloride was used as the quenching agent. The dark green reaction mixture gave a brown oil on work-up. On cooling in an acetone /cardice bath, a dark solid precipitated. This procedure was repeated several times and the mother liquor concentrated in vacuo. The product was purified by column chromatography on silica, using hexane as the eluent. Yield after purification, 0.35g, (6.6%). ν_{\max} (neat film/cm⁻¹) 665, 740, 848, 915, 1040, 1135, 1250, 1395, 1635, 2810 -3115. ¹³C NMR (400MHz, CDCl₃) δ -1.76, -0.83 (2xSiMe₃), 32.20 (CH₃), 32.79 (-CH₂-) 48.31 (CHSi), 124.17 (CH₂=C), 152.08 (CH₂=CSi) 209.94 (CO). MS (EI+) *m/e* 271, 256,198,172,73. Analysis calc'd for C₁₃H₂₉NSi₂O: Cald. C 57.5 H 10.6 Found C 57.0, H 10.6

5.3.4. Triethyl 3-trimethylsilylbut-3-ene-1,1,1-tricarboxylate (36)

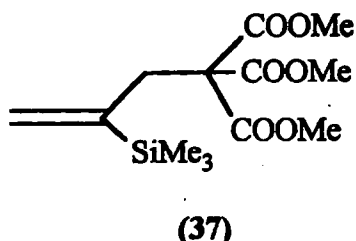


(36)

Quenching the α -lithiovinyltrimethyl silane with ethylchloroformate and work- up as described in section 7.3.1, above gave triethyl-3-trimethylsilylbut-3-ene-1,1,1-tricarboxylate 36, 3.8g (65%) yield. ν_{\max} (neat film/cm⁻¹) 3040 (C-H_{str} alkene), 2960 (C-H_{str} alkane), 1750 (C=O), 1680 (C=C_{str}), 1270 (C-O), 1150 (C-O-C), 860 (C-H_{def} OOP CH₂=C). ¹H NMR (400 MHz, CDCl₃) δ 0.07 (s, 9H, SiMe₃), 1.24 (t, J=14.2 Hz, 3H, CH₃), 2.98 (s, 2H, CH₂), 4.22 (q, J=14.2 Hz, 2H, CH₂CH₃), 5.41 and 5.58 (d, J=1.8Hz, 1H and d, 1.8Hz, 1H, CH₂=C); ¹³C NMR (400 MHz, CDCl₃) δ -1.03 (SiMe₃), 14.55 (CH₃), 37.32 (CH₂), 62.68 (OCH₂), 126.80 (CH₂=), 146.92 (CSi), 167.33 (CO).

^{29}Si NMR (400 MHz, CDCl_3) δ -2.10. Analysis calc'd for $\text{C}_{16}\text{H}_{28}\text{Si}_1\text{O}_6$: Cald. C 55.8 H 8.2; Found C 55.8 H 8.6.

5.3.5 Trimethyl 3-trimethylsilylbut-3-ene-1,1,1-tricarboxylate(37)



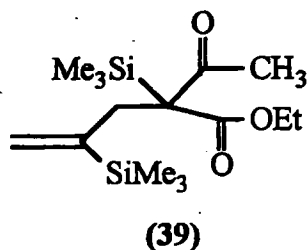
When the reaction was carried out using methyl chloroformate as the acylating agent, Trimethyl 3-trimethylsilylbut-3-ene-1,1,1-tricarboxylate 37 was isolated in 3.8g (74%), yield.

ν_{max} (neat film/ cm^{-1}) 3040 (C-H_{str} alkene), 2960 (C-H_{str} alkane), 1750 (C=O), 1680 (C=C), 1270 (C-O_{str}), 1150 (C-O-C), 860 (C-H_{def}). ^1H NMR (400 MHz, CDCl_3) δ 0.06 (s, 9H, SiMe_3), 2.99 (s, 2H, CH_2), 3.74 (s, 9H, 3xOMe), 5.41 and 5.54 (d, $J=1.6\text{Hz}$, 1H and d, 1.6Hz, 2H, $\text{CH}_2=\text{C}$); ^{13}C NMR (400 MHz, CDCl_3) δ -1.03 (SiMe_3), 37.39 (CH_2), 53.76 (OCH_3), 127.11 ($\text{CH}_2=$), 147 (CSi), 167.67 (CO), 175.88 (C); ^{29}Si NMR (400 MHz, CDCl_3) δ -1.96; Analysis calc'd for $\text{C}_{13}\text{H}_{22}\text{SiO}_6$: Cald. C 59.1 H 9.7 Found C 58.9 H 9.9. Calculated (M- CH_3)=287.09509, Measured (M- CH_3)=287.09974

5.4. Reaction of α , β -unsaturated trimethylsilyl keto-enolates with carbonyl compounds.

This section describes the reaction of the α -lithiovinyltrimethylsilane with α -trimethylsilylvinyl ketone and the subsequent reaction of the resultant enolate with water and carbonyl compounds. The carbonyl compounds used were acetic anhydride, alkyl chloroformates and acetaldehyde. The reaction condition employed were similar in all cases. The reaction with ethyl chloroformate as the acylating agent of the enolate is representative.

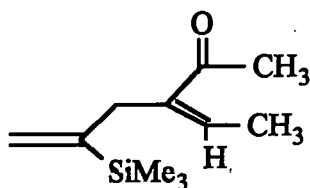
5.4.1. Ethyl 2-oxo-3,5-bis(trimethylsilyl)hex-5-en-3-carboxylate (39)



α -Lithiovinyltrimethylsilane was generated as shown in section 5.3.1 using α -bromovinyltrimethylsilane (3.04g, 0.017mole). To this cold yellow solution, was added dropwise of α -trimethylsilylvinylmethyl ketone (2.45g, 0.017mole) in a little dry THF whilst the temperature was maintained at -100°C . The mixture was stirred for a further 20mins. at -100°C , before allowing it to gradually warm up to -20°C . Ethylchloroformate (0.025 mole) was then added dropwise and the reaction mixture slowly allowed to warm up to room-temperature. It was further stirred for 17hrs, before aqueous hydrolysis at 0°C with saturated ammonium chloride solution. The organic layer was extracted using diethylether and dried with anhydrous magnesium sulphate.

121.73 (CSi), 123.76 (CH₂=), 149.86 (=CSi), 151.36 (COOR), 154.10 (CO); ²⁹Si NMR (400 MHz, CDCl₃) δ -3.25; MS (EI+) *m/e* 300 (1), 285 (1), 224 (3), 221 (2), 209 (4), 153 (4), 149 (7), 137 (38), 136 (30), 135 (5), 133 (3), 97 (12), 89 (24), 73 (100), 59 (19), 45 (13), 29 (1)

5.4.3 3-Ethylidene-5-trimethylsilyl-hex-5-ene-2-one (41)

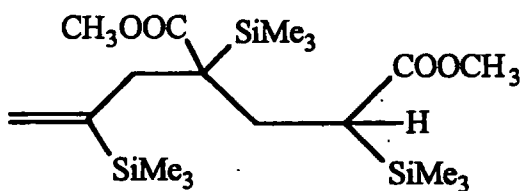


(41)

Reacting the keto-enolate with acetaldehyde, gave after purification 2.1g, (63%) of the diene: ν_{max} (neat film/cm⁻¹) 3040 (C-H_{def} alkene), 2960 (C-H_{def} alkane), 1670 (C=O), 1640 (C=C), 1440 (C-H_{def} CH₃CO), 1250 (SiMe₃), 860 (C-H_{def} OOP alkene). ¹H NMR (400 MHz, CDCl₃) δ 0.12 (s, 9H, SiMe₃), 1.78 (d, J=7.0 Hz, 3H, CH₃), 2.29 (s, 3H, COCH₃), 3.09 (s, 2H, -CH₂-), 5.22 (d, J=1.94, 1H, CH₂H_b=), 5.4 (d, J=1.94 Hz, 1H, CH₂H_b=), 6.92 (q, J=7.0 Hz, 1H, CH); ¹³C NMR (400 MHz, CDCl₃) δ -1.23 (SiMe₃), 15.57 (CH₃), 26.25 (OCH₃), 30.49 (CH₂), 122.92 (CH₂=), 140.50 (CH=), 149.17 (=CSi), 199.55 (CO); ²⁹Si NMR (400 MHz, CDCl₃) δ -2.86; MS (EI+) *m/e* 196 (1), 181 (15), 149 (24), 73 (100), 57 (15), 43 (19), 29 (4); Analysis calc'd for C₁₁H₂₀SiO: Cald. C 67.2 H 10.2; Found C 67.2 H 10.2.

5.5 Reaction of α , β -unsaturated trimethylsilyl ester-enolates with carbonyl compounds.

5.5.1. Dimethyl 1,3,5-tris(trimethylsilyl)hex-5-ene-1,3-dicarboxylate (43)

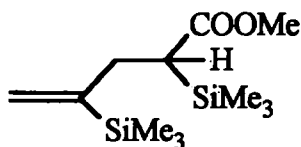


(43)

To the cold solution of α -lithiovinyltrimethylsilane generated from (3.04g, 0.017mole) of α -bromovinyltrimethylsilane as described in section 5.3.1, was added dropwise trimethylsilyl acrylate (0.017mole) in a little dry THF. The mixture was stirred for a further 30 mins at -100°C . Methylchloroformate (0.025mole) was then added dropwise and the mixture allowed to warm up to room temperature and stirred continuously for a further 17 hrs.

Aqueous work-up, gave a mixture of the mono- and di-esters. Purification over silica using hexane/ether as eluent gave the diester and monoester in 4.6g (65%) and 0.85g (19%) yield respectively. Diester(43): ν_{max} (neat film/ cm^{-1}) 3040 ($\text{C-H}_{\text{str alkene}}$), 2906 ($\text{C-H}_{\text{str alkane}}$), 1750 (C=O, -COOR), 1608 (C=C), 1430 ($\text{C-H}_{\text{def alkane}}$), 1250 (SiMe_3), 1200, 840 ($\text{C-H}_{\text{def alkene}}$). ^1H NMR (400 MHz, CDCl_3) δ 0.13 (s, 9H, SiMe_3), 0.16 (s, 9H, SiMe_3), 0.17 (s, 9H, SiMe_3), 2.11-2.77 (m, 5H, $-\text{CH}_2\text{CCH}_2\text{CH}-$), 3.65 (s, 3H, OCH_3), 3.69 (s, OCH_3), 5.52-5.42 (m, 2H, $\text{CH}_2=$); ^{13}C NMR (400 MHz, CDCl_3) δ -2.07, -1.78, -1.03. ($3\times\text{SiMe}_3$), 29.93 ($-\text{CH}_2-$), 36.04 (CHSi), 51.40 (OCH_3), 51.54 (OCH_3), 124.68 ($\text{CH}_2=$), 148.6 ($=\text{CSi}$), 176 (COOR), 177 (COOR); MS (EI^+) m/e 416 (0.3), 401 (1), 343 (0.6), 218 (39), 203 (11), 183 (12), 167 (19), 147 (13), 109 (15), 89 (25), 73 (100), 59 (17), 45 (22); Analysis calc'd for $\text{C}_{19}\text{H}_{40}\text{Si}_3\text{O}_4$: Cald. C 54.8 H 9.7; Found C 54.8 H 9.7

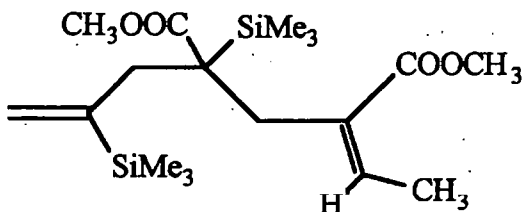
Methyl-2,4-bis(trimethylsilyl)prop-4-enoate (44)



(44)

ν_{\max} (neat film/ cm^{-1}) 3040(C-H_{str} alkene), 2960 (C-H_{str} alkane), 1750(C=O , -COOR), 1680(C=C), 1270 (SiMe_3), 1200 (C-O_{str}). ^1H NMR (400 MHz, CDCl_3) δ 0.00 (s, 18H, $2 \times \text{SiMe}_3$), 2.50-2.57 (m, 3H, $\text{CH}_2\text{-CH-}$), 3.52 (s, 3H, OCH_3), 5.21 and 5.48 (d, $J=1.94$, 1H and d, $J=1.94\text{Hz}$, 1H, $\text{CH}_2=\text{C}$); ^{13}C NMR(400 MHz, CDCl_3) δ -1.44 (SiMe_3), 0.22 (SiMe_3), 33.10 (OCH_3), 37.62 ($\text{CH}_2\text{-}$), 52.19 (CH-), 124.79 ($\text{CH}_2=\text{}$), 152.65 (CSi), 176.55 (CO); ^{29}Si NMR (400 MHz, CDCl_3) δ -3.80; MS (EI^+) m/e 243($-\text{CH}_3$) (5), 189 (2), 159 (4), 149 (9), 114 (10), 105 (9), 99 (10), 88 (13), 73 (54), 69 (25), 57 (23), 45 (16), 43 (26), 41 (25), 28 (100); Analysis calc'd for $\text{C}_{12}\text{H}_{26}\text{Si}_2\text{O}_2$: Cald. C 55.8 H 10.1; Found C 55.2 H 10.0;

5.5.2 Dimethyl 5,7-bis(trimethylsilyl)octa-2,7-diene-3,5-dicarboxylate (45)



(45)

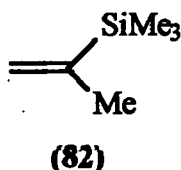
To the cold solution of the α -lithiovinyltrimethylsilane, generated from 3.04g of α -bromo vinyltrimethylsilane as described in section 5.3.1, was added trimethylsilylacrylate, (0.017mole) at -100°C . The mixture was stirred at this temperature for a further 30 mins. before dropwise addition of excess acetaldehyde. Hydrolytic work up by pouring the mixture into an aqueous solution of ammonium chloride after 17 hrs. at room-temperature, and extraction with ether gave the diene **45**, 4.15g (66%) yield after purification by column chromatography on silica gel using, hexane/ethyl acetate as the eluent. We did not confirm the stereochemistry of the alkene. ν_{max} (neat film/ cm^{-1}) 3040($\text{C-H}_{\text{str alkene}}$), 2940 ($\text{C-H}_{\text{str alkane}}$), 1750 (C=O), 1680 (C=C) 1430 (C-H_{str}), 1250 (SiMe_3), 1200, 840 ($\text{C-H}_{\text{def alkene}}$). ^1H NMR (400 MHz, CDCl_3) δ 0.07 (s, 9H, SiMe_3), 0.08 (s, 9H, SiMe_3), 1.86 (d, $J=7.3$ Hz, 3H, CH_3), 2.29-2.92 (m, 4H, $\text{CH}_2\text{-C-CH}_2\text{-}$), 3.58 (s, 3H, OCH_3), 3.69 (s, 3H, OCH_3), 5.33-5.38 (dd, $J=1.72, 1.72$ Hz, 2H, $\text{CH}_2\text{=}$), 6.04 (q, $J=7.3$ Hz, 1H); ^{13}C NMR (400 MHz, CDCl_3) δ - 1.01 (SiMe_3), 0.88 (SiMe_3), 16.40 (CH_3), 35.74 (OCH_3), 35.85 (OCH_3), 51.54 (CH_2), 51.71(CH_2), 123.96 ($\text{CH}_2\text{=C}$), 131.99 (C=CHCH_3), 139.99(CSi), 148.84 (C), 169.52(C), 177.26(CO); ^{29}Si NMR (400 MHz, CDCl_3) δ -2.88, 12.34; MS (EI+) m/e 355($-\text{CH}_3$) (0.7), 323 (1), 271 (2), 257 (5), 207 (4), 197 (2), 183 (9), 167 (15), 153 (10), 147 (10), 117 (10), 105 (9), 89 (28), 73 (100), 59 (14), 45 (10); Analysis calc'd for $\text{C}_{18}\text{H}_{34}\text{Si}_2\text{O}_4$: Cald. C 58.3 H 9.4; Found C 58.4 H 9.4.

5.6 Reactions of bistrimethylsilyl-alkenes with electrophilic reagents.

The reactions of bistrimethylsilylalkenes and the electrophilic reagents (hydrogen chloride gas, hydrogen bromide gas, trifluoroacetic acid) were performed in an Nmr tube under similar conditions and no attempt was made to isolate any of the products. All Nmr spectra were consistent with authentic samples. The reaction of the bistrimethylsilyl propenes with hydrogen chloride gas is representative.

5.6.1 Reaction of 2,3-bistrimethylsilylpropene with hydrogen chloride gas.

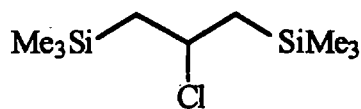
To 2,3-bistrimethylsilylpropene (0.186g, 0.001mole) in an nmr tube was added deuteriated chloroform (CDCl_3) and the mixture shaken to ensure mixing. Dry hydrogen chloride gas was bubbled into the tube for about 5 minutes. The Nmr spectrum of the resulting mixture was then measured and shown the product to be isopropenyl trimethylsilane¹¹, **82**.



^1H NMR (400 MHz, CDCl_3) δ 0.09 (s, 9H, SiMe_3), 1.82 (s, 3H, $-\text{CH}_3$), 5.24 (dd, 1H, $J_1=1.6\text{Hz}$, $J_2=3.6\text{Hz}$, $\text{CH}_2=$), 5.54 (dd, 1H, $J_1=2.4\text{Hz}$, $J_2=2.4\text{Hz}$, $\text{CH}_2=$); ^{13}C NMR (400 MHz, CDCl_3) δ -2.16 (SiMe_3), 22.22 (CH_3), 124.45 (CH_2), 147.68 ($=\text{CSi}$).

5.6.2 Reaction of 1,3-bistrimethylsilylpropene with hydrogen chloride gas.

Similar reaction conditions with 1,3-bistrimethylsilylpropene gave 2-chloro-1,3-bistrimethylsilylpropane **88**.



(88)

^1H NMR (400 MHz, CDCl_3) δ 0.027 (s, 9H, SiMe_3), 0.03 (s, 9H, SiMe_3), 1.68 (d, 4H, $J=1.2\text{Hz}$, $2 \times \text{CH}_2\text{Si}$), 4.31 (m, 1H, $-\text{CHCl}-$); ^{13}C NMR (400 MHz, CDCl_3) δ -1.62 (SiMe_3), -0.96 (SiMe_3), 31.02 (CH_2Si), 31.57 (CH_2Si), 57.94 (CCl).

With prolonged passage of the HCl gas, the addition product collapsed and only signals corresponding to allyltrimethylsilane¹² 84 were present.



(84)

^1H NMR (400 MHz, CDCl_3) δ 0.02 (s, 9H, SiMe_3), 1.70 (d, 2H, $J=0.8\text{Hz}$, CH_2Si), 6.09 (m, 3H, $\text{CH}_2=\text{CH}-$); ^{13}C NMR (400 MHz, CDCl_3) δ -2.05 (SiMe_3), 21.27 (CH_2Si), 131.69 ($=\text{CH}$), 134.66 ($\text{CH}_2=$).

5.7.

Synthesis of β -silylsubstituted aziridines

5.7.1

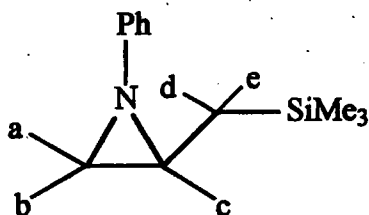
Synthesis of silylaziridines by thermolysis.

The reaction of phenyl azide¹³ with allylsilanes under thermolytic conditions was employed to form N-phenyl-2-(trimethylsilyl)methyl aziridine, N-phenyl -*cis*-2-(trimethylsilyl)methyl-3-pentyl aziridine, N-phenyl-2-(dimethylphenylsilyl)methyl aziridine, N-phenyl-2-(triphenylsilyl)methyl aziridine. These compounds were purified by flash chromatography over neutral activated alumina, with extensive decomposition. Micro-scale distillation resulted in most cases in polymerisation and / or re-arrangement of the aziridines. The synthesis of N-phenyl-2-(trimethylsilyl) methyl aziridine, described in section 5.7.1.1, as representative.

5.7.1.1

N-phenyl-2-(trimethylsilyl)methylaziridine (52)

Phenyl azide (2.03g, 0.17mol) and allyltrimethylsilane (3.9g, 0.34mol) were placed in a round bottomed flask and stirred under reflux for 20hrs. The dark yellow solution was washed in brine, extracted with ether and evaporated. The product was distilled in vacuo to give a pale-yellow oil, 2.60g (74.3%): b.pt. 80-85°C/0.005mmHg;

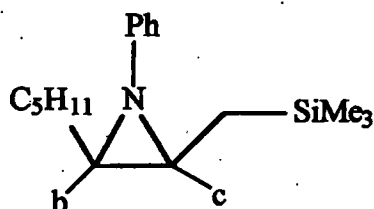


(52)

ν_{\max} (neat film/cm⁻¹) 2954.4, 1599.3, 1491.9, 1385.1, 1292.9, 1249.6, 861.01. ¹H NMR (400 MHz, CDCl₃) δ 0.09 (s, 9H, SiMe₃), 0.59 (s_b, 1H, H_d) and 1.23 (dd, 1H, H_e, J₁=4.8Hz, J₂=14.8Hz), 1.95 (d, 1H, H_a, J=3.2Hz), 2.09 (d, 1H, H_b, J=6.0Hz), 2.15 (m, 1H, H_c), 6.85-7.35 (m, 5H, Ph); ¹³C NMR (400 MHz, CDCl₃) -0.59 (SiMe₃), 21.83 (CH₂Si), 35.53 (CH₂), 37.98 (CH), 121.72, 122.35, 129.61, 156.14 (Ph).

5.7.1.2 N-phenyl-*cis*-2-(trimethylsilyl)methyl-3-pentyl aziridine (53)

Similar reaction and work-up conditions were carried out for the reaction of *cis*-2-methyltrimethylsilyl-3-pentene (0.25g, 0.014mol) and phenyl azide (0.08g, 0.006mole) to give, 0.14g (77%) of *cis*-2-methyltrimethylsilyl-3-pentyl-N-phenylaziridine as a colourless oil.



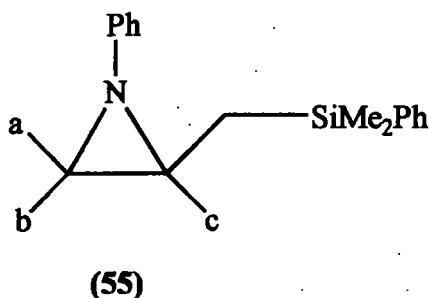
(53)

¹H NMR (400 MHz, CDCl₃) δ -0.03 (s, 9H, SiMe₃), 0.48 (d, 2H, J=7.6Hz, CH₂Si), 0.86 (s, 1H, H_b), 0.88 (m, 3H, CH₃), 1.11 (m, 8H, (CH₂)₄), 1.28 (s_b, 1H, H_e), 6.80-7.40 (m, 5H, Ph). ¹³C NMR (400 MHz, CDCl₃) δ -1.64(SiMe₃), 14.10 (CH₃), 16.69 (CH₂Si), 22.72, 23.91, 31.85, 33.60, (CH₂)₄ 28.78 (CH(CH₂)₄), 29.43 (CHCH₂Si), 119.00, 124.86, 129.76, 159.00 (Ph); MS (EI⁺) *m/e* 276 (16), 259 (12), 199 (36), 176 (49), 73 (100), 59 (25), 43 (22).

5.7.1.3

N-phenyl-2-(dimethylphenylsilyl)methyl aziridine (55)

Reacting phenyl azide (0.83g, 0.007mol) and allyldimethylphenylsilane, (1.23g, 0.007mol) gave the product, N-phenyl-2-(dimethylphenylsilyl)methyl aziridine, 1.0g (55%) as a pale yellow oil.

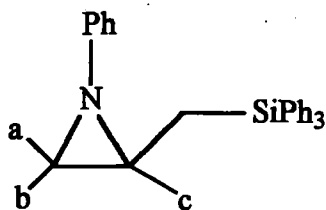


ν_{\max} (neat film/ cm^{-1}) 3040, 2960, 1605, 1500, 1490, 1275, 1125, 850, 650. ^1H NMR (400 MHz, CDCl_3) δ 0.04 (s, 6H, SiMe_2), 0.53 and 1.51 (s_b , and dd 1H, $J_1=5.2\text{Hz}$, $J_2=14.8\text{Hz}$, CH_2Si), 2.32 (d, 1H, H_a , $J=3.2\text{Hz}$), 2.46 (d, 1H, H_b , $J=6.4\text{Hz}$), 2.55 (m, 1H, H_c), 6.90-7.57 (m, 10H, 2xPh); ^{13}C NMR (400 MHz, CDCl_3) δ 0.85 (SiMe_2), 20.36 (CH_2Si), 35.29 (CH_2ring), 36.64 (CHring), 120.82, 121.98, 128.78, 128.88 132.98, 133.55, 138.45, 139.80 (2xPh); Analysis calc'd for $\text{C}_{17}\text{H}_{21}\text{Si}_1\text{N}$: Calcd. C 76.4 H 7.9 Found C 76.3 H 7.8.

Calculated M= 267.14432, Measured M = 267.13800

5.7.1.4 **N-phenyl-2-triphenylsilylmethyl aziridine (56)**

Reaction of phenyl azide (0.60g, 0.005mol) with allyltriphenylsilane (0.15g, 0.005mol) gave N-phenyl-2-triphenylsilylmethyl aziridine as a white solid, 0.10g (51%) yield m.p. 222°C.



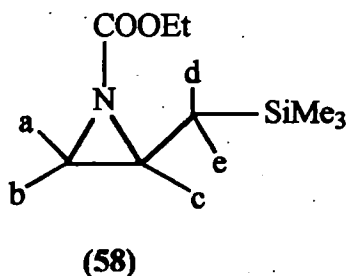
(56)

^1H NMR (400 MHz, CDCl_3) δ 2.14 (d, 2H, $J_1=6.8\text{Hz}$, $J_2=15.2\text{Hz}$ CH_2Si), 2.98 (dd, 1H, H_a , $J_1=3.9\text{Hz}$, $J_2=15.6\text{Hz}$ and 3.05 (dd, 1H, H_b , $J_1=6.8\text{Hz}$, $J_2=15.6\text{Hz}$ CH_2), 4.42 (m, 1H, H_c , CH), 7.24-7.58 (m, 20H, 4xPh); ^{13}C NMR (400 MHz, CDCl_3) δ 26.01 (CH_2Si), 55.16 (CH_2), 63.68 (CH), 129-155(4xPh).

5.8 Synthesis of trimethylsilyl aziridines from azidoformates by the photolytic method.

A mixture of ethyl azidoformate and allylsilanes were placed in a quartz tube with continuous stirring. The tube was irradiated to give the corresponding N-carboethoxy silyl-aziridines. A large amount of polymeric material is produced and their isolation and subsequent purification extremely difficult. This method was used for allyltrimethylsilane, allyldimethylphenylsilane, allyltriphenylsilane, *cis*-2-methyltrimethylsilyl-3-pentylpropene and *trans*-2-methyltrimethylsilyl-3-phenylpropene. Proton NMR of all the silanes used except the latter showed the presence of the corresponding aziridines, but any attempt to separate the mixture by flash chromatography or distillation led only unidentified material. Thus only the reaction with allyltrimethylsilane is reported here.

Allyltrimethylsilane (4.6g, 0.04mol) was placed in a quartz tube for irradiation. To this was added over 8 days, ethyl azidoformate, in four equal portions of 1.15g (0.01mol), during the irradiation process. Vacuum distillation of the crude orange mixture gave 2.5g (31%) of pure 1-carboethoxy-2-trimethylsilylmethyl aziridine.



ν_{\max} (neat film/ cm^{-1}) 3040, 2986, 2898, 1750, 1425, 1400, 1300, 1250, 1210, 1100, 900. ^1H NMR (400 MHz, CDCl_3) δ 0.07 (s, 9H, SiMe_3), 0.50 and 1.06 (dd, 1H, H_a , $J_1=7.6$, $J_2=14.0\text{Hz}$, and dd, 1H, H_b , $J_1=8.0$ $J_2=14.8\text{Hz}$, CH_2Si), 1.25 (t, 3H, $J=6.8\text{Hz}$, OCH_2CH_3), 1.88 (d, 1H, H_a , $J=4.0\text{Hz}$), 2.30 (d, 1H, H_b , $J=6.0\text{Hz}$), 2.43 (m, 1H, CH), 4.13 (q, 2H, $J=6.8\text{Hz}$, OCH_2CH_3); ^{13}C NMR (400MHz, CDCl_3) δ -1.55 (SiMe_3), 15.24 (CH_3), 20.22 (CH_2Si), 33.13 (CH_2), 35.94 (CH_c), 63.25 (OCH_2), 164.56 (CO); MS (EI^+) m/e 202 (1), 186 (5), 172 (2), 158 (8), 140 (11), 128 (20), 112 (10), 103 (18), 100 (20), 97 (19), 75 (28), 74 (10), 73 (100), 61 (10), 59 (18), 45 (15), 43 (10), 41 (18).

5.9

Synthesis of N-unsubstituted silyl-aziridines

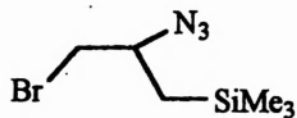
This class of aziridines were synthesized by the lithium aluminium hydride reduction of alkyl silylbromo azides which were themselves synthesised by the addition of bromine azide to the corresponding allylsilanes in dichloromethane. The reaction mixture was worked up by hydrolysis with 20% sodium hydroxide solution. In all cases, this gave a mixture of the cyclised product (aziridine) and the reduced product (silylated amine). Attempt to separate often resulted in the decomposition of the aziridine.

General procedures for the synthesis of silylbromoazides from allylsilanes

Similar preparative methods were used in the preparation of silyl bromoazides from, allyltrimethylsilane, allyldimethylphenyl silane and allyltriphenyl silane. The reaction with allyltrimethylsilane is a representative.

5.9.1 1-Trimethylsilyl-2-azido-3-bromopropane (59a)

Bromine (8.00g, 0.05mol) was added dropwise to an ice-cooled mixture of sodium azide (3.25g, 0.05mol) in dry dichloromethane (100ml) containing 30% hydrochloric acid (25 ml). The mixture was stirred for a further 45 mins. The organic layer containing the bromine azide was decanted from the semi-solid aqueous layer and added dropwise to a stirred, cooled (-5°C) solution of allyltrimethylsilane (5.7g, 0.05mol) in dichloromethane. The mixture was stirred for a further 45 mins at 0°C. Washing with two 50ml portions of dilute sodium bicarbonate solution was followed by removal of the solvent using a rotary evaporator at room temperature and purification by chromatography with silica gel using hexane as the eluent to give the bromine azide adduct (59a) as a colourless oil, 6.0g, (51%):

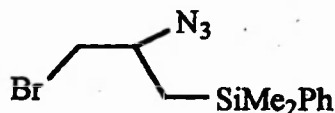


(59a)

^1H NMR (400 MHz, CDCl_3) δ 0.09 (s, 9H, SiMe_3), 0.93 (dd, 2H, $J_1=6.0\text{Hz}$, $J_2=8.8\text{Hz}$, CH_2Si), 3.47 (dd, 2H, $J_1=6.4\text{Hz}$, $J_2=10.0\text{Hz}$, CH_2Br), 3.62 (m, 1H, CHN_3); ^{13}C NMR (400 MHz, CDCl_3) δ -1.22 (SiMe_3), 21.09 (CH_2Si), 34.19 (CH_2Br), 60.54 (CHN_3); MS (EI+) m/e 195.16 (5.9, $(-\text{N}_3)$), 193.09 (6.2), 156.21 (2.9), 139.12 (6.6), 100 (13), 73.18 (100), 59.20 (21), 41.20 (60.9), 28.29 (11.2); Analysis calc'd for $\text{C}_6\text{H}_{14}\text{Si}_1\text{N}_3\text{Br}$: C 30. 5; H 5. 9; N, 17. 8; found: C 30. 5; H 5. 9; N 17. 6.

5.9.2 1-Dimethylphenylsilyl-2-azido-3-bromopropane (59b)

Reaction of bromine azide (1.2g, 0.01mol) with allyldimethylphenyl silane (1.76g, 0.01mole) gave the corresponding 1-dimethylphenylsilyl-2-azido-3-bromopropane 2.5g, (84%).



(59b)

ν_{max} (neat film/ cm^{-1}) 3040, 2906, 2150, 1500, 1475, 1300, 1125, 800, 600, 550. ^1H NMR (400 MHz, CDCl_3) δ -0.02 and 0.00 (2s, 6H, SiMe_2), 0.77 and 0.86 (dd, 2H, $J_1=8.8\text{Hz}$, $J_2=14.7\text{Hz}$ and $J_1=5.4\text{Hz}$, $J_2=14.7\text{Hz}$ (CH_2Si), 2.99 (m, 2H, CH_2Br), 3.16 (m, 1H, CHN_3), 6.98-7.12 (m, 5H, Ph); ^{13}C NMR (400 MHz, CDCl_3) δ -2.42-2.15 (SiMe_2), 20.71 (CH_2Si), 38.16 (CH_2Br), 60.32 (CHN_3), 128.06, 129.43, 133.47, 137.33(Ph). MS (EI+) m/e 255 (0.2, - N_3), 176 (46), 162 (48), 149 (46), 135 (100), 119 (23), 107 (15), 105 (18), 92 (10), 91 (11), 77 (4), 57 (3), 42 (16), 28 (4)

5.9.3 1-Triphenylsilyl-2-azido-3-bromopropane (59c)

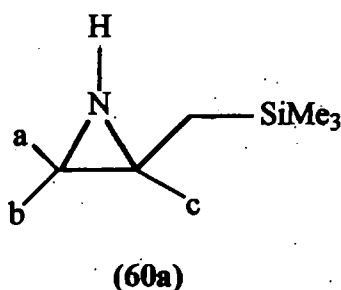
Similar reaction condition with allyltriphenylsilane (3.0g, 0.01mole) and bromine azide (1.2g, 0.01mole) gave 1-triphenylsilyl-2-azido-3-bromopropane as a solid, 4.0g (95%): ^1H NMR (400 MHz, CDCl_3) δ 1.91(dd, 2H, $J_1=8.8\text{Hz}$, $J_2=15.2\text{Hz}$, CH_2Si), 3.46 (dd, 2H, $J_1=4.4\text{Hz}$, $J_2=16\text{Hz}$, CH_2Br), 3.79 (m, 1H, CHN_3); ^{13}C NMR (400 MHz, CDCl_3) δ 18.44 (CH_2Si), 38.12 (CH_2Br), 60.12 (CHN_3), 127.85, 130.03, 135.70, 146.44 (3xPh); MS (EI+) m/e 379 (0.6, (- N_3)), 340 (0.7), 300 (25), 273 (29), 259 (100), 224 (12), 199 (13), 181 (27), 167 (3), 155 (11), 105 (20), 91 (4), 77 (10), 65 (1), 53 (7), 28 (2). Analysis calc'd for $\text{C}_{21}\text{H}_{20}\text{Si}_1\text{N}_3\text{Br}$: Calcd. C 59.7 H 4.8 N 9.9; Found C 59.4 H 4.9 N 9.3

5.9.4 General procedure for the synthesis of N-unsubstituted silyl aziridines.

The procedure below for the synthesis of 2-trimethylsilylmethyl aziridine describes in details the synthesis of N unsubstituted silylaziridines from the silylbromoazido adduct by reduction with lithium aluminium hydride.

5.9.4.1 2-trimethylsilylmethyl aziridine (60a)

A slurry of lithium aluminium hydride (1.67g, 0.043mol) in dry ether (30ml) was cooled in an ice-salt bath with stirring under nitrogen. 2-Bromo-1-methyltri-methylsilyl-1-azidoethane (3.47g, 0.015mol) in dry ether (5ml) was added dropwise during 10min, carefully maintaining the temperature below 0°C. Weak effervescence (N₂) was accompanied by the production of a pale olive green colour. The mixture was stirred for a further 45mins. at 0°C and then allowed to warm to room temperature. Stirring was continued for a further 17 hrs. Re-cooling to 0°C was followed by slow hydrolysis with 9ml of 20% sodium hydroxide, added dropwise with stirring over a period of 15mins. After warming to room temperature, the mixture was stirred rapidly for 45mins. The resultant fine granular solid was washed well with ether and the mother liquor and washings were carefully dried with magnesium sulfate for several hours. Concentration gave 2.4g of a colourless, oily product. Purification by flash column chromatography on silica-gel, using hexane as the eluent, was accompanied by substantial decomposition, giving 0.8g (44%) of the aziridine.



¹H NMR (400 MHz, CDCl₃) δ 0.04 (s, 9H, SiMe₃), 0.35 and 0.99 (dd, 1H, J₁=8.4Hz, J₂=14.0Hz and dd, 1H, J₁=5.2, J₂=14.0Hz, CH₂Si), 1.10 (d, 1H, H_a, J=5.8Hz) and 1.73 (d, 1H, H_b, J=5.8Hz, CH₂), 1.91 (m, 1H, H_c, CH);

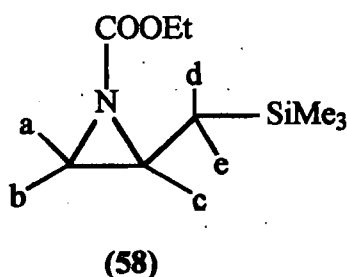
¹³C NMR (400 MHz, CDCl₃) δ 0.85 (SiMe₃), 22.65 (CH₂Si), 26.65 (CH₂N), 27.22 (CH).

Analysis calc'd for $C_6H_{15}Si_1N_1$: Calcd. C 55.8 H 11.7 N 10.8; Found C 55.6 H 11.7 N 10.7

1-Triphenylsilyl-2-azido-3-bromopropane (59c) gave a mixture of products and attempt to purify by flash chromatography led to decomposition.

5.9.5 Acylation of N-unsubstituted-silylaziridine

To a solution of 2-trimethylsilylmethylaziridine (60a), (0.18g, 0.0014mol) dry ether 30ml was added triethylamine (0.14g, 0.0014mol). A solution of ethylchloroformate (0.14g, 0.0013mol) in 5ml ether was added dropwise with stirring under cooling in an ice-salt bath. After the addition was complete, stirring was continued for 30 mins., then triethyl amine hydrochloride was removed by filtration and solvent removed under vacuum to give 0.22g (79%) of N-Carboethoxy-2-methyltrimethylsilyl aziridine (58).



1H NMR (400 MHz, $CDCl_3$) δ 0.07 (s, 9H, $SiMe_3$), 0.50 and 1.06 (dd, 1H, H_d , $J_1=7.6$, $J_2=14.0$ Hz, and dd, 1H, H_e , $J_1=8.0$, $J_2=14.8$ Hz, CH_2Si), 1.25 (t, 3H, $J=6.8$ Hz, OCH_2CH_3), 1.88 (d, 1H, H_a , $J=4.0$ Hz, CH_2), 2.30 (d, 1H, H_b , $J=6.0$ Hz, CH_2), 2.43 (m, 1H, CH), 4.13 (q, 2H, $J=6.8$ Hz, OCH_2CH_3); ^{13}C NMR (400MHz, $CDCl_3$) δ -1.55 ($SiMe_3$), 15.24 (CH_3), 20.22 (CH_2Si), 33.13 (CH_2), 35.94 (CH_c), 63.25 (OCH_2), 164.56 (CO).

The data was consistent with that of an authentic sample synthesized via a different route (see section 5.5.2)

5.9.6

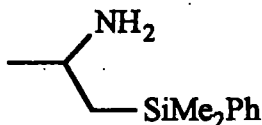
Synthesis of β -amino alkylsilanes

The following β -amino alkylsilanes were synthesized from the reduction of the corresponding silylbromoazido adduct with lithium aluminium hydride as described in section 5.9.3.4.1 but the subsequent hydrolysis with sodium hydroxide solution was done at room temperature. Quantitative amounts of the products were isolated and purified by column chromatography.

5.9.6.1

2-amino-1-dimethylphenylsilylpropane (61b)

Reduction of 1-Dimethylphenylsilyl-2-azido-3-bromopropane **59b** (4.47g, 0.015mol) with a slurry of lithium aluminium hydride (1.67g, 0.043mol) in dry ether (30ml) gave 1.85g (64%) yield of the product.



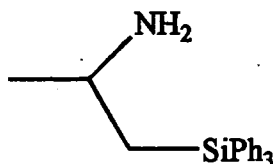
(61b)

ν_{\max} (KBr film/ cm^{-1}) 3000 (N-H_{str}), 1600 (N-H_{def}), 1450, 1425, 1225, 1180, 1150, 1050, 850, 780, 725. ^1H NMR (400 MHz, CDCl_3) δ 0.29 (s, 6H, SiMe_2), 1.28 (d, 3H, $\text{J}=6.4\text{Hz}$, CH_3), 1.45 (dd, 2H, $\text{J}_1=2.4\text{Hz}$, $\text{J}_2=14\text{Hz}$, CH_2Si), 4.73 (m, 1H, CHN), 7.48 (m, 5H, Ph); ^{13}C NMR δ -2.53, -2.29 (SiMe_2), 21.27 (CH_3), 23.80 (CH_2Si), 47.39 (CHN), 127.76, 128.35, 133.78, 136.91(Ph); MS (EI^+) m/e 193 (44), 178 (8), 165 (5), 149 (13), 135 (100), 105 (17), 89 (20), 77 (6), 57 (21), 44 (83), 28 (11). Calculated (M^+-NH) = 178.11779, Measured (M^+-NH) = 178.10194

5.9.6.2

2-amino-1-triphenylsilylpropane(61c)

Using 1-Triphenylsilyl-2-azido-3-bromopropane **59c** (6.34g, 0.015mol) and of lithium aluminium hydride (1.67g, 0.043mol) gave 3.2g (68%) yield of the product **61c**



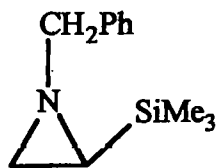
(**61c**)

^1H NMR (400 MHz, CDCl_3) δ 1.08 (d, 3H, $J=6.0\text{Hz}$, CH_3), 1.61 (dd, 2H, $J_1=4.4\text{Hz}$, $J_2=6.4\text{Hz}$, CH_2Si), 3.30 (dd, 1H, $J_1=6.4\text{Hz}$, $J_2=12.4\text{Hz}$, CHN), 7.56 (m, 15H, 3xPh); ^{13}C NMR δ 25.31 (CH_2Si), 27.71 (CH_3), 44.14 (CHN), 127.71, 129.36, 135.66 (3xPh); MS (EI+) m/e 316 (3), 302 (3), 259 (77), 240 (12), 224 (14), 198 (62), 181 (39), 155 (12), 105 (30), 73 (15), 57 (50), 53 (8), 44 (100), 28 (6); Calculated $M=317.15997$, Measured $M=317.15756$.

Slightly different reaction conditions were employed for the synthesis of the trimethylsilyl- and the non-silylaziridines.

5.10.1 2-Trimethylsilyl-benzylaziridine (92)¹⁵

To a stirred solution of 1-trimethylsilyl-ethylene-1,2-cyclic sulfate (0.5g, 0.0025mol) in dried THF (25ml) was added benzylamine (0.55g, 0.005mol) slowly under a nitrogen atmosphere. Stirring was continued for 24 hours at room temperature. The solution was cooled to -78°C and *n*-BuLi solution in hexane (1.24ml, 0.003mol, 2.5M) was added and stirring continued for another 2 hours. The resulting solution was diluted with dried ether (50 ml), filtered through a pad of silica gel and concentrated. The product was purified by flash chromatography to give 0.15g, (27% yield) of pure aziridine.

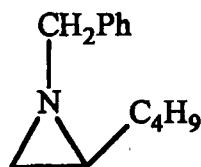


(92)

ν_{max} (neat film/ cm^{-1}) 3031, 2956, 2924, 1496, 1454, 1247, 1027, 1012, 854, 839, 752.

^1H NMR (400MHz, CDCl_3) δ -0.12 (s, 9H, SiMe_3), 0.50 (dd, 1H, $J_1=4.7$ Hz, $J_2=7.7$ Hz, CH), 1.46 (d, 1H, $J=7.7$ Hz, CH_2), 1.72 (d, 1H, $J=4.7$ Hz, CH_2), 2.89 (d, 1H, $J=13.2$ Hz, CH_2Ph), 3.86 (d, 1H, $J=13.2$ Hz, CH_2Ph), 7.21-7.32 (m, 5H, Ph); ^{13}C NMR (400MHz, CDCl_3) δ -3.19 (SiMe_3), 28.57 (CHSi), 31.83 (CH_2), 67.56 (CH_2Ph), 126.87, 128.12, 128.21, 139.71 (Ph); MS(EI+) m/e 205 (3, M), 204 (8, M-H^+), 190 (11, M-CH_3), 114 (100, $\text{M-CH}_2\text{Ph}$), 91 (58, CH_2Ph), 86 (46, HCSiMe_3), 73 (70, SiMe_3).

To a stirred solution of 1-*n*-butylethylene-1,2-cyclic sulfate (0.9g, 0.005mol) in dry THF (50ml) was added benzylamine (1.07g, 0.001mol). After refluxing for 8 hrs at 60°C, the reaction mixture was cooled to room temperature and *n*-BuLi, (4.8ml, 0.0012mol, 2.5M in hexane) was slowly added. The resultant pale yellow solution was stirred at room temperature for 2hrs. and then diluted with 50ml ether, washed with water (2x20ml), brine (20ml) and dried over anhydrous magnesium sulfate. Removal of the solvent and purification by column chromatography over silica gel gave 2-butyl-1-benzylaziridine 0.70g, (74%), as an oil.



(94)

ν_{max} (neat film/cm⁻¹) 2957, 2929, 2898, 1575, 1454, 1430, 1300, 1210, 1100, 733. ¹H NMR (400 MHz, CDCl₃) δ 0.78 (t, 3H, CH₃), 1.19-1.42(m, 6H, (CH₂)₃), 1.53 (d, 2H, J = 2.9Hz), 1.62 (m, 1H), 3.28 (dd, 2H, J₁=13.2 Hz, J₂=13.6Hz, -CH₂-), 7.19-7.27 (m, 5H, Ph). ¹³C NMR (400 MHz, CDCl₃) δ 14.03 (CH₃), 22.42, 29.57, 32.68, (CH₂)₃, 34.06 (CH₂N), 39.80 (CHPh), 64.98 (-CH₂Ph), 126.94, 128.15, 128.28 139.94 (Ph). MS (EI+) *m/e* (190, 18, MH⁺), 176 (32), 146(5), 134 (7), 120 (4), 106 (19), 91(100), 77 (7), 65 (7), 41(5), 28 (18).

The following silylaziridines : *cis* -1-propyl-2-trimethylsilyl-3-phenylaziridine **67**, *trans*-1-phenyl-2-trimethylsilyl-3-phenylaziridine **68** and *cis*-1- phenyl-2-trimethyl silyl-3-phenylaziridine **69** were all prepared by the literature method¹⁷. They were all subjected to the same reaction conditions with the following activated alkenes and alkynes, acetylene dicarboxylate, maleic anhydride and diethyl maleate. The reaction of *trans*-1- phenyl-2-trimethylsilyl-3-phcnylaziridine **69** with diethylacetylene dicarboxylate is a representative.

5.11.1 Reaction of silylaziridine with diethylacetylene dicarboxylate

To a solution of *trans*-1-phenyl-2-trimethylsilyl-3-phenylaziridine **69** (0.5g, 0.0019mol) in 25ml dry toluene was added diethylacetylene dicarboxylate (0.32g, 0.0019mol) and the mixture refluxed for 4hrs. The mixture was cooled and the solvent removed by rotary evaporator to give brown solid. Proton nmr of this crude sample showed no trimethyl silyl peaks and attempt to purify by column chromatography gave an oily brown residue which could not be identified.

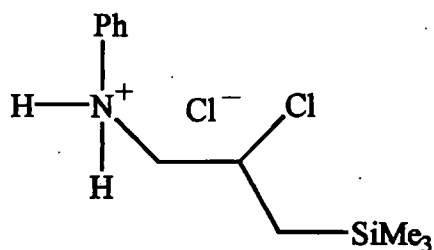
5.12.1 Formation of products containing a carbon-halogen bond.

Ring opening with reagents such as hydrogen chloride gas, trimethylsilyl chloride, trimethylsilyl bromide and ethyl chloroformate all gave products with a new carbon - halogen bond .

5.12.1.1 Reaction of N-phenyl-2-(trimethylsilyl)methylaziridine with hydrogen chloride gas.

The procedure below for the reaction of N-phenyl-2-(trimethylsilyl)methylaziridine describes the general method employed for the ring-opening of all the aziridines with hydrogen chloride gas.

N-phenyl-2-(trimethylsilyl)methylaziridine, **52** (0.50g, 0.0024mol), was dissolved in 5ml of dry ether and 2ml of dry benzene. Gaseous hydrogen chloride was passed slowly through this solution at room temperature, for a period of about 10 minutes. The solution developed a heavy white precipitate and was allowed to stand at room temperature overnight. The product was removed by filtration and washed with hexane to afford a white solid, 2-chloro-1-trimethylsilyl-N-phenylpropylamine hydrochloride **114** 0.45g (66%). The solid was very moisture sensitive and decomposed at room temperature after few hours to give a brown tar.

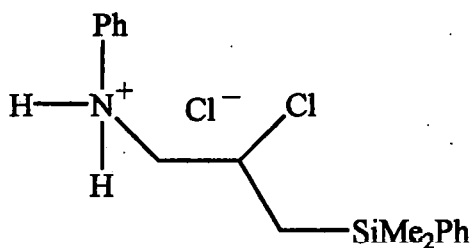


(114)

^1H NMR (400 MHz, CDCl_3) δ 0.006 (s, 9H, SiMe_3), 1.20 (dd, 2H, $J_1=9.2\text{Hz}$, $J_2=14.4\text{Hz}$, CH_2Si), 3.54 (d, 2H, $J=6.8\text{Hz}$, CH_2N), 4.33 (m, 1H, CHCl), 7.41 (m, 5H, Ph); ^{13}C NMR (400 MHz, CDCl_3) δ 0.26 (SiMe_3), 26.11 (CH_2Si), 55.21 (CH_2N), 61.52 (CHCl), 124.56, 130.89, 131.07, 135.84 (Ph).

5.12.1.2 Reaction of N-phenyl-2-(dimethylphenylsilyl)methylaziridine with hydrogen chloride gas.

Using the procedure described in 5.11.1.1, N-phenyl-2-(dimethylphenylsilyl)methylaziridine (0.50g, 0.0019mol) was reacted with hydrogen chloride gas, to give 2-chloro-1-dimethylphenylsilylpropylamine hydrochloride 117, (85% yield, determined by proton nmr).



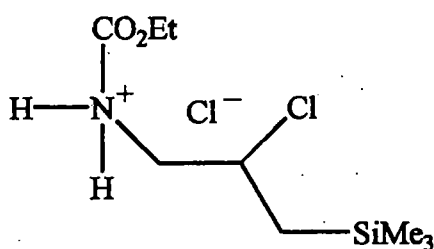
(117)

^1H NMR (400 MHz, CDCl_3) δ 0.22 (s, 6H, SiMe_2), 1.46 (dd, 2H, $J_1=3.6\text{Hz}$, $J_2=6.8\text{Hz}$, CH_2Si), 3.41 (dd, 2H, $J_1=4.8\text{Hz}$, $J_2=8.4\text{Hz}$, CH_2N), 4.25 (m, 1H, CHCl), 7.43 (m, 10H, 2xPh); ^{13}C NMR (400 MHz, CDCl_3) δ 0.83 (SiMe_2), 24.92 (CH_2Si), 54.65 (CHCl), 59.16 (CH_2N), 122.44, 123.48, 128.0, 129.4, 129.9, 132.9, 133.5, 137, 138 (2xPh).

No further analysis was possible because of the ease of decomposition and high moisture sensitivity of the product.

5.12.1.3 Reaction of N-carbethoxy-2-(trimethylsilyl)methylaziridine with hydrogen chloride.

Using the procedure described in 5.12.1.1, N-carbethoxy-2-(trimethylsilyl)methylaziridine (0.30g, 0.0015mol) with hydrogen chloride gas to give 2-chloro-1-trimethylsilyl-N-carbethoxypropylamine hydrochloride **118**, (70%, as determined by proton nmr). The reaction was much faster and hence the reaction time was reduced to 5 minutes, as prolonged passage of hydrogen chloride gas gave the corresponding salt of allylamine.

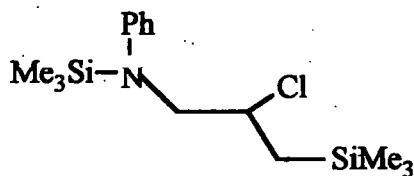


(118)

^1H NMR (400 MHz, CDCl_3): δ 0.064 (s, 9H, SiMe_3), 1.17 (dd, 2H, $J_1=3.6\text{Hz}$, $J_2=14.8\text{Hz}$, CH_2Si), 1.23 (t, 3H, $J=4.4\text{Hz}$, CH_3), 3.13-3.66 (m, 2H, CH_2N), 4.14 (q, 2H, $J=4.4\text{Hz}$, OCH_2), 5.13 (m, 1H, CHCl); ^{13}C NMR (400 MHz, CDCl_3) δ 0.25 (SiMe_3), 15.52(CH_3), 26.46 (CH_2Si), 51.02 (CH_2N), 61.96 (OCH_2), 62.44 (CHCl), 157.47(CO).

5.12.1.4 Reaction of N-phenyl-2-(trimethylsilyl)methylaziridine with trimethylsilylchloride

A solution of N-phenyl-2-(trimethylsilyl)methylaziridine (0.1g, 0.5mmol) in deuterated chloroform (1ml) was placed in a 5mm nmr. tube. Trimethylsilyl chloride (0.05g, 0.48mmol) was added dropwise. After addition, the nmr tube was shaken thoroughly and left to stand at room temperature for 5 minutes to give 2-chloro-1-trimethylsilyl-N-trimethylsilylpropylamine 120, (95% as determined by nmr). Attempted purification by column chromatography and distillation on a bigger scale using a Kugelrohr apparatus only gave products of decomposition.



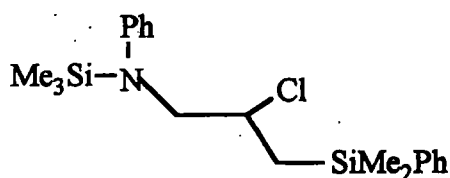
(120)

^{13}C NMR (400 MHz, CDCl_3) 0.31(SiMe_3), 26.41(CH_2Si), 56.67(CH_2N), 59.56(CHCl), 118.08, 122.31, 130.30, 143.87 (Ph).

5.12.1.5 Reaction of N-phenyl-2-(dimethylphenylsilyl)methylaziridine with trimethylsilylchloride

A solution of N-phenyl-2-(dimethylphenylsilyl)methylaziridine (0.1g, 0.37mmol) in deuterated chloroform (1ml) was placed in a 5mm nmr. tube. Trimethylsilyl chloride (0.05g, 0.48mmol) was added dropwise. After addition, the nmr tube was shaken thoroughly and left to stand at room temperature for 5 minutes to give 2-chloro-1-dimethylphenylsilyl-N-trimethylsilylpropylamine 121, (60% as determined by n.m.r).

Attempted purification by column chromatography and distillation on a bigger scale using a Kugelrohr apparatus only gave products of decomposition. The nmr of the crude product is given below:

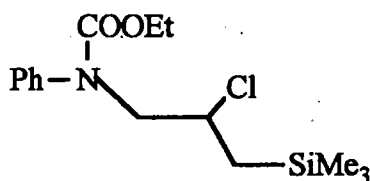


(121)

^1H NMR (400 MHz, CDCl_3) δ 0.07 (s, 9H, SiMe_3), 0.08 (s, 6H, SiMe_2), 1.45 (t, 2H, $J=8.4\text{Hz}$, CH_2Si), 3.42 (dd, 2H, $J_1=8.8\text{Hz}$, $J_2=11.6\text{Hz}$, CH_2N), 4.25 (m, CHCl), 7.3-7.5 (m, 10H, 2xPh); ^{13}C NMR (400 MHz, CDCl_3) δ 0.15 (SiMe_3), 0.48 (SiMe_2), 26.87 (CH_2Si), 56.12 (CH_2N), 61.66 (CHCl), 125.21, 129.67, 131.04, 132.07, 135.11, 139.07, 141.78), (2xPh).

5.12.1.6 Reaction of N-phenyl-2-(trimethylsilyl)methylaziridine with ethylchloroformate

A solution of N-phenyl-2-(trimethylsilyl)methyl aziridine (0.1g, 0.48mmol) in deuterated chloroform (1ml) was placed in a 5mm nmr tube. Ethylchloroformate (0.05g, 0.48mmol) was added dropwise. After addition, the nmr. tube was shaken thoroughly and left to stand at room temperature for 5 minutes to give 2-chloro-1-trimethylsilyl-N-phenyl-N-carboethoxypropylamine **122**, (92% as determined by nmr). Attempted purification by column chromatography and distillation on a bigger scale using a Kugelrohr apparatus only gave products of decomposition.



(122)

ν_{\max} (neat film/cm⁻¹) 2950, 2200, 1700, 1580, 1550, 1450, 1400, 1375, 1250, 900, 850, 750.
¹H NMR (400 MHz) δ 0.04 (s, 9H, SiMe₃), 1.14 (t, 3H, J=7.3Hz, CH₃), 1.22 (d, 2H, J=6.8Hz, CH₂Si), 3.87 (d, 2H, J=6.4Hz, CH₂N), 4.18 (q, 2H, J=7.3Hz, CH₂CH₃), 4.34 (m, 1H, CHCl), 7.2-7.38 (m, 5H, Ph); ¹³C NMR (400 MHz, CDCl₃) δ 0.00 (SiMe₃), 15.39 (CH₃), 25.93 (CH₂), 59.45 (CHCl), 62.56 (CH₂N), 62.71 (CH₂O), 127.70 128.36, 129.82, 142.08 (Ph), 156.67 (CO); MS (EI+) m/e 313 (4), 277 (4), 248 (3), 204 (13), 192 (9), 178 (65), 165 (11), 150 (8), 134 (18), 132 (14), 106 (94), 93 (24), 77 (29), 73 (100), 65 (11), 59 (18), 45 (22), 43 (13), 41 (22), 29 (47).

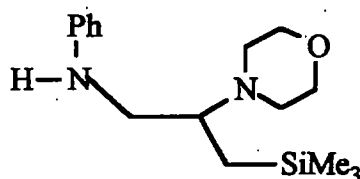
5.12.2

Formation of products containing C-N bond.

Ring opening reactions were carried out with the following nitrogen nucleophiles resulting in the ring opened products in which the nitrogen nucleophile becomes attached to one of the aziridine carbons.

5.12.2.1 Reaction of N-phenyl-2-(trimethylsilyl)methylaziridine with morpholine

N-phenyl-2-(trimethylsilyl)methylaziridine (1.0g, 4.8mmol) was added to a stirred solution of morpholine (0.84, 9.6 mmol) in 25ml dry carbon tetrachloride, containing a catalytic amount of ammonium chloride (0.05g, 1mmol). The mixture was heated at 55°C for 12 hrs. The carbon tetrachloride was removed using a rotatory evaporator to leave a dark brown residue. The residue was purified by chromatography using silica gel and hexane-dichloromethane as the eluent. After elution of excess morpholine, an oily product, 2-morpholino-1-trimethylsilyl-N-phenylpropylamine **125**, was obtained. 0.7g (70%).



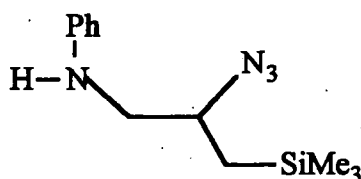
(125)

ν_{\max} (neat film/cm⁻¹) 3075, 2980, 1600, 1500, 1450, 1325, 1250, 1210, 1120, 910, 855, 845, 750, 690. ¹H NMR (400 MHz, CDCl₃) : δ 0.00 (s, 9H, SiMe₃), 0.96 (dd, 2H, $J_1=3.2$ Hz, $J_2=14.8$ Hz, CH₂Si), 2.4-2.8 (m, 8H, -N(CH₂)₄O-) 3.09 (m, 1H, CHN), 3.76 (db, 2H, CH₂N),

6.6-7.1 (m, 5H, Ph); ^{13}C NMR (400 MHz, CDCl_3) δ 0.00 (SiMe_3), 23.21 (CH_2Si), 46.70 (CH_2N), 51.37 (CHN), 68.21 (CH_2O), 113.93, 118.08, 130.11, 149.28 (Ph); MS (EI^+) m/e 292 (0.4), 277 (0.9), 265 (0.5), 241 (0.9), 206 (2), 192 (35), 186 (100), 106 (16), 77 (10), 73 (94), 59 (6), 45 (12), 28 (5); Analysis calc'd for $\text{C}_{16}\text{H}_{28}\text{Si}_1\text{O}_1\text{N}_2$: Calcd: C 65.7 H 9.7. Found: C 66.1 H 9.3.

5.12.2.2 Reaction of N-phenyl-2-(trimethylsilyl)methylaziridine with sodium azide

N-phenyl-2-(trimethylsilyl)methylaziridine (1.0g, 4.8mmol) was added to a stirred suspension of sodium azide (0.94g, 14.4mmol) in 25 ml DMF. The mixture was heated at 55°C overnight. The DMF was removed using a rotatory evaporator to leave a residue which was hydrolysed with water and extracted with diethyl ether. The organic layer was dried using anhydrous MgSO_4 . The filtered solution was concentrated and purified by chromatography using silica gel and hexane-dichloromethane as the eluent to give the addition product as a mixture of two isomers 0.7g (58%). We did not attempt to separate the isomers, however from proton nmr, 2-azido-1-trimethylsilyl-N-phenyl propylamine **126** was found to be the major isomer (75%).

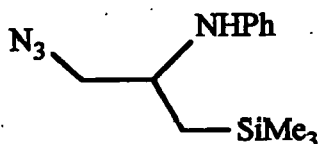


(126)

ν_{\max} (neat film/ cm^{-1}) 3400, 2980, 2100, 1600, 1500, 1320, 1250, 855, 845, 750, 680

^1H NMR (400 MHz, CDCl_3) δ 0.00 (s, 9H, SiMe_3), 0.83 (dd, 1H, $J_1=6.8\text{Hz}$, $J_2=14.4\text{Hz}$) and 0.88 (dd, 1H, $J_1=7.6\text{Hz}$, $J_2=14.4\text{Hz}$, CH_2Si), 3.09 (dd, 1H, $J_1=8.8\text{Hz}$, $J_2=13.2\text{Hz}$) and 3.35 (dd, 1H, $J_1=4.8\text{Hz}$, $J_2=10.8\text{Hz}$, CH_2NH), 3.69 (m, 1H, CHN_3), 3.96 (sb, 1H, NH), 6.52-7.24 (m, 5H, Ph); ^{13}C NMR (400 MHz, CDCl_3) δ 0.00 (SiMe_3), 21.05 (CH_2Si), 51.24 (CH_2NH), 60.64 (CHN_3), 114.02, 118.98, 130.46, 148.46 (Ph). MS (EI+) m/e 248 (M, 5), 206 (M- N_3 , 2), 192 (13), 106 (100), 77 (12), 73 (24), 59 (5), 45 (5), 28 (2).

3-azido-1-trimethylsilyl-N-phenylpropylamine, **127** (minor isomer, 25%).



(127)

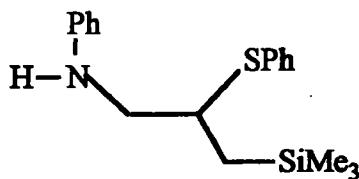
^1H NMR (400 MHz, CDCl_3) δ 0.00 (s, 9H, SiMe_3), 0.83 (dd, 1H, $J_1=6.8\text{Hz}$, $J_2=14.4\text{Hz}$) and 0.88 (dd, 1H, $J_1=7.6\text{Hz}$, $J_2=14.4\text{Hz}$, CH_2Si), 3.33 (dd, 1H, $J_1=4.8\text{Hz}$, $J_2=8.2\text{Hz}$) and 3.65 (dd, 1H, $J_1=4.8\text{Hz}$, $J_2=9.7\text{Hz}$, CH_2N_3), 3.96 (m, 1H, CHN), 6.52-7.24 (m, 5H, Ph); ^{13}C NMR (400 MHz, CDCl_3) δ 0.12 (SiMe_3), 22.47 (CH_2Si), 51.31 (CHN), 57.64 (CH_2N_3), 114.20, 118.76, 130.46, 147(Ph).

5.12.3 Formation of products containing a Carbon-Sulphur bond.

The aziridines were reacted with thiophenol and sodium thiophenolate to give ring opened products that contain the sulphur nucleophiles attached to one of the aziridine carbons.

5.12.3.1 Reaction of N-phenyl-2-(trimethylsilyl)methylaziridine with thiophenol

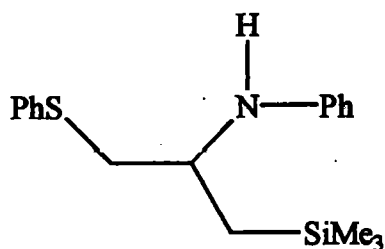
N-phenyl-2-(trimethylsilyl)methylaziridine (1.0g, 4.8mmol) was added to a stirred suspension of thiophenol (1.05g, 9.6mmol) in dry carbon tetrachloride (25ml). The mixture was heated at 55°C overnight. The carbon tetrachloride was removed using a rotatory evaporator to leave a dark brown residue. The residue was purified by chromatography using silica gel and hexane-dichloromethane as the eluent. After elution of excess thiophenol, an oily product, 1.2g (80%), was isolated as a mixture of two isomers, with 2-thiophenyl-1-trimethylsilyl-N-phenylpropylamine **128**, being the major product (80% determined by proton nmr):



(128)

ν_{\max} (neat film/cm⁻¹) 3475, 2952, 1602, 1504, 1475, 1465, 1300, 1248, 1179, 1152, 1135, 1110, 862, 837, 787, 746, 691, 614. ¹H NMR (400 MHz, CDCl₃) δ 0.019 (s, 9H, SiMe₃), 0.80 (dd, 1H, $J_1=9.6$ Hz, $J_2=15.2$ Hz) and 1.24 (dd, 1H, $J_1=4.4$ Hz, $J_2=15.2$ Hz, CH₂Si), 2.88 (dd, 1H, $J_1=6.8$ Hz, $J_2=12.8$ Hz) and 3.10 (dd, 1H, $J_1=6.4$ Hz, $J_2=12.7$ Hz, CH₂N), 3.65 (m, 1H, CHSPh), 6.38-6.69 (m, 5H, SPh), 7.47 (m, 5H, Ph); ¹³C NMR (400 MHz, CDCl₃) δ 0.22 (SiMe₃), 23.69 (CH₂Si), 43.13 (CH₂N), 50.97 (CHS), 114.07, 118.47, 127.53, 128.61, 148.98 (SPh), 129.88, 130.20, 131.53, 134.18, 147.61(Ph); MS (EI+) m/e 315 (7), 218 (16), 209 (12), 192 (94), 184 (9), 176 (7), 165 (3), 150 (16), 106 (45), 77 (12), 73 (100), 65 (10), 59 (6), 45 (12), 39 (5). Analysis calc'd for C₁₈H₂₅Si₁S₁N₁: Calcd: C 68. 5 H 8. 0 S 10. 2; Found: C 68. 7 H 8. 6 S 9. 5.

3-Thiophenyl-1-trimethylsilyl-N-propylamine 129 (minor isomer, 20%)



(129)

^1H NMR (400 MHz, CDCl_3) δ 0.08 (s, 9H, SiMe_3), 1.01 (dd, 2H, $J_1=4.0\text{Hz}$, $J_2=8.0\text{Hz}$, CH_2Si), 1.51 (sb, NH), 3.21 (dd, 2H, $J_1=4.0\text{Hz}$, $J_2=13.2\text{Hz}$, CH_2S), 3.42 (m, 1H, CHN), 6.38-6.69 (m, SPh), 7.1-7.4 (m, 5H, NPh); ^{13}C NMR (400 MHz, CDCl_3) δ 0.41 (SiMe_3), 22.37 (CH_2Si), 46.98 (CHN), 50.29 (CH_2S), 114.07, 118.42, 127.53, 128.61, 148.98 (SPh), 129.88, 130.20, 131.53, 134.18, 147.61(NPh).

5.12.3.2 Reaction of N-phenyl-2-(trimethylsilyl)methylaziridine with sodium thiophenolate

Sodium thiophenolate was prepared by adding sodium (5mmol) to thiophenol (5mmol) in methanol (20ml) under a nitrogen atmosphere. The mixture was stirred at room temperature until all the sodium was consumed. To this mixture was added 5 mmol of N-phenyl-2-(trimethylsilyl)methylaziridine and the mixture refluxed for 2 hrs. Excess thiophenol and methanol were removed using a rotatory evaporator, to leave a residue which was taken up in water and extracted using diethyl ether. The organic layer was dried using anhydrous MgSO_4 . Removal of the solvent gave product 2-thiophenyl-1-trimethylsilyl-N-phenylpropylamine 128, 1.2g, (80%).

ν_{max} (neat film/ cm^{-1}) 3475, 2952, 1602, 1504, 1475, 1465, 1300, 1248, 1179, 1152, 1135, 1110, 862, 837, 787, 746, 691, 614. ^1H NMR (400 MHz, CDCl_3) δ 0.019 (s, 9H, SiMe_3), 0.80 (dd, 1H, $J_1=9.6\text{Hz}$, $J_2=16.0\text{Hz}$) and 1.24 (dd, 1H, $J_1=4.4\text{Hz}$, $J_2=14.4\text{Hz}$, CH_2Si), 2.88 (dd, 1H, $J_1=6.8\text{Hz}$, $J_2=12.8\text{Hz}$) and 3.10 (dd, 1H, $J_1=6.4\text{Hz}$, $J_2=12.7\text{Hz}$, CH_2N), 3.65 (m, 1H, CHSPH), 6.38-6.69 (m, 5H, SPH), 7.47 (m, 5H, Ph); ^{13}C NMR (400 MHz, CDCl_3) δ 0.22 (SiMe_3), 23.69 (CH_2Si), 43.13 (CH_2N), 50.97 (CHS), 114.07, 118.47, 127.53, 128.61, 148.98 (SPH), 129.88, 130.20, 131.53, 134.18, 147.61(Ph); MS (EI^+) m/e 315 (7), 218 (16), 209 (12), 192 (94), 184 (9), 176 (7), 165 (3), 150 (16), 106 (45), 77 (12), 73 (100), 65 (10), 59 (6), 45 (12), 39 (5)

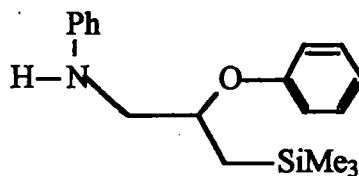
The product was found to have a similar isomer composition to when only thiophenol was used.

5.12.4 Formation of products containing a Carbon-Oxygen bond.

The silyl-substituted aziridines were reacted with phenols and *p*-cresol to give ring opened products in which the oxygen nucleophiles becomes attached to one of the aziridine carbons.

5.12.4.1 Reaction of N-phenyl-2-(trimethylsilyl)methylaziridine with phenol

N-phenyl-2-(trimethylsilyl)methylaziridine (1.0g, 4.8mmol) was added to a stirred suspension of phenol (0.9g, 9.6 mmol) in 25ml. dry carbon tetrachloride. The mixture was heated at 55°C for 12hrs. The carbon tetrachloride was removed using a rotatory evaporator to leave a dark brown residue. The residue was purified by chromatography using silica gel and hexane-dichloromethane as the eluent. After elution of excess phenol, an oil, 2-phenoxy-1-trimethylsilyl-N-phenylpropylamine **115** was obtained 1.0g (76%).

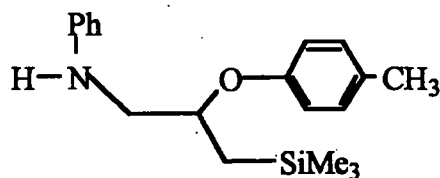


(132)

ν_{\max} (neat film/ cm^{-1}) 3410, 3050, 2980, 1600, 1500, 1250, 1075, 1030, 920, 850, 750, 700.
 ^1H NMR (400 MHz, CDCl_3) δ 0.00 (s, 9H, SiMe_3), 1.05 (dd, 1H, $J_1=7.6\text{Hz}$, $J_2=14.6\text{Hz}$) and 1.26 (dd, 1H, $J_1=6.0\text{Hz}$, $J_2=14.6\text{Hz}$, CH_2Si), 3.29 (dd, 1H, $J_1=6.8\text{Hz}$, $J_2=12.8\text{Hz}$ and), 3.45 (dd, 1H, $J_1=2.8\text{Hz}$, $J_2=12.8\text{Hz}$, CH_2N), 4.68 (m, 1H, CHOPh), 6.5-6.8 (m, 5H, OPh), 7.18 (m, 5H, Ph); ^{13}C NMR (400 MHz, CDCl_3) δ 0.87 (SiMe_3), 21.52 (CH_2Si), 50.05 (CH_2N), 75.29 (CHOPh), 113.40, 116.67, 118.36, 148.00 (Ph), 120.77, 129.86, 130.26, 158.25 (OPh); MS (EI^+) m/e 299 (8), 206 (15), 166 (11), 151 (39), 132 (22), 106 (97), 94 (20), 77 (28), 73 (100), 65 (13), 59 (6), 51 (10), 45 (14), 39 (18), 28 (10) Analysis calc'd for $\text{C}_{18}\text{H}_{25}\text{Si}_1\text{O}_1\text{N}_1$: Calcd: C 72.2 H 8.4 N 4.7; Found C 72.7 H 8.0 N 4.1

5.12.4.2 Reaction of N-phenyl-2-(trimethylsilyl)methylaziridine with *p*-Cresol.

N-phenyl-2-(trimethylsilyl)methylaziridine (1.0g, 4.8mmol) was added to a stirred suspension of *p*-Cresol (1.0g, 9.6 mmol) in 25ml dry carbon tetrachloride. The mixture was heated at 55°C for 12hrs. The carbon tetrachloride was removed using a rotatory evaporator to leave a dark brown residue. The residue was purified by chromatography using silica gel and hexane-dichloromethane as the eluent. After elution of excess *p*-cresol, and purification using column chromatography, an oil, 2-cresol-1-trimethylsilyl-N-phenylpropylamine 133 was obtained 1.2g(79%)



(133)

ν_{\max} (neat film/cm⁻¹) 3475, 2960, 1610, 1510, 1250, 920, 850, 750. ¹H NMR (400 MHz, CDCl₃) δ 0.08 (s, 9H, SiMe₃), 1.03 (dd, 1H, $J_1=8.0\text{Hz}$, $J_2=14.4\text{Hz}$) and 1.24 (dd, 1H, $J_1=6.0\text{Hz}$, $J_2=14.4\text{Hz}$, CH₂Si), 2.29 (s, 3H, CH₃), 3.25 (dd, 1H, $J_1=6.8\text{Hz}$, $J_2=12.8\text{Hz}$, CH₂N), 3.39 (d, 1H, $J=12.8\text{Hz}$, CHN), 4.02 (sb, 1H, NH), 4.61 (m, 1H, CHOPh), 6.21-6.80 (m, 4H, OPh), 7.02-7.2 (m, 5H, Ph); ¹³C NMR (400 MHz, CDCl₃) δ 0.00 (SiMe₃), 21.15 (CH₃), 21.56 (CH₂Si), 49.99 (CH₂N), 75.51 (CHO), 113.64, 116.69, 118.19, 148.79 (Ph), 129.88, 130.70, 136.11, 156.05 (OPh); MS (EI⁺) m/e 313 (7), 206 (25), 207 (17), 190 (11), 180 (39), 165 (100), 150 (10), 132 (15), 106 (54), 91 (18), 77 (20), 73 (84), 65 (8), 59 (8), 45 (11), 27 (3). Analysis calc'd for C₁₉H₂₇Si₁O₁N₁: Calcd: C 72.8 H 8.7 N 4.5; Found C 73.0 H 8.6 N 4.7;

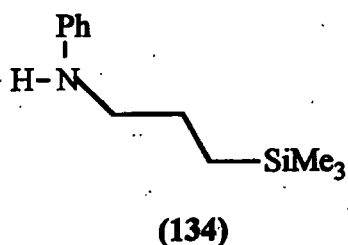
5.12.5

Ring-opening using reducing agents

The following reducing agents were employed; lithium aluminium hydride, sodium hydride, sodium borohydride. Ring-opening was observed only with lithium aluminium hydride and sodium borohydride.

5.12.5.1 Reaction of N-phenyl-2-(trimethylsilyl)methylaziridine with lithium aluminium hydride

A slurry of lithium aluminium hydride (0.26g, 7.2mmol) in 20ml dry ether under nitrogen was cooled in an ice-salt bath with stirring. To this was added dropwise in dry ether (2ml), N-phenyl-2-(trimethylsilyl)methylaziridine (0.5g, 2.4mmol). The mixture was allowed to warm up to room temperature and stirred for a further 17hrs. Hydrolysis with water, was followed by extraction with diethyl ether and the organic layer dried with anhydrous magnesium sulphate. The filtrate was concentrated and purified using silica gel with hexane-dichloromethane as the eluent to give 1-trimethylsilyl-N-phenyl propylamine **134**(0.35g, 71%).



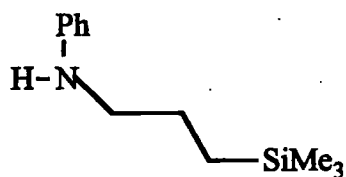
^1H NMR (400 MHz, CDCl_3) δ 0.07 (s, 9H, SiMe_3), 0.55 (t, 2H, $J=8.32\text{Hz}$, CH_2Si), 1.61 (m, 2H, $\text{C-CH}_2\text{-C}$), 3.07 (t, 2H, $J=8.32\text{Hz}$, CH_2N), 3.62 (sb, 1H, NH), 7.16 (m, 5H, Ph); ^{13}C NMR (400 MHz, CDCl_3) δ -0.46 (SiMe_3), 15.29 (CH_2Si), 25.33 ($-\text{CH}_2-$), 48.48 (CH_2N), 113.93, 118.28, 130.46, 149.72 (Ph); MS (EI+) m/e 189 (23), 158 (15), 147 (7), 117 (12), 101 (8), 84 (6), 73 (100), 59 (11), 45 (12), 29 (3).

Calculated $M=207.1443$; measured $M=207.1446$

5.12.5.2

Reaction of N-phenyl-2-(trimethylsilyl)methylaziridine with sodium Borohydride.

A mixture of sodium borohydride (0.26g, 6.8mmol) in 20ml dry carbon tetrachloride and N-phenyl-2-(trimethylsilyl)methylaziridine (0.5g, 2.4mmol), under nitrogen were refluxed with stirring for 12hrs. The mixture was cooled to room temperature and then hydrolysed with water. Hydrolysis with water, was followed by extraction with diethyl ether and the organic layer dried with anhydrous magnesium sulphate. The filtrate was concentrated and purified using silica gel with hexane-dichloromethane as the eluent to give 1-trimethylsilyl-N-phenylpropylamine **134** 0.25g (50%).

**(134)**

^1H NMR (400 MHz, CDCl_3) δ 0.07 (s, 9H, SiMe_3), 0.55 (t, 2H, $J=8.32\text{Hz}$, CH_2Si), 1.611 (m, 2H, C- CH_2 -C), 3.07 (t, 2H, $J=8.32\text{Hz}$, CH_2N), 3.62 (sb, 1H, NH), 7.16 (m, 5H, Ph); ^{13}C NMR (400 MHz, CDCl_3) δ -0.46 (SiMe_3), 15.29 (CH_2Si), 25.33 ($-\text{CH}_2-$), 48.48 (CH_2N), 113.93, 118.28, 130.46, 149.72 (Ph); MS (EI+) m/e 189 (23), 158 (15), 147 (7), 117 (12), 101 (8), 84 (6), 73 (100), 59 (11), 45 (12), 29 (3).

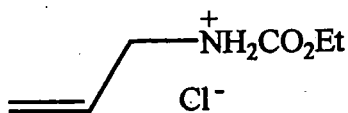
No further analysis was necessary as the product had already been characterised in section 5.12.5.1.

The reaction of silylaziridines with sodium methoxide, sodium phenoxide, trimethylsilyl triflate, trifluoro acetic acid, trifluoromethanesulphonic acid, tetrabutyl ammonium fluoride, boron-trifluoride etherate and copper iodide all gave allylamine. The reaction conditions varied and hence the experimental conditions applied for each reagent are detailed below. Reaction of N-carboethoxysilylaziridine with excess hydrogen chloride gas also gave the allylamine.

5.12.6.1

Reaction of N-carboethoxysilylaziridine with excess HCl (g)

Excess hydrogen chloride was passed through a solution of N-carboethoxy-2-(trimethylsilylmethylaziridine (0.30g, 0.0015mol) in a 5 ml tube containing deuterated chloroform for about 10 minutes to give the corresponding N-carboethoxyallylamine hydrogen chloride salt (0.25g, 100%). Deuterated Chloroform was removed under vacuum and the product characterized without further purification.



^1H NMR (400 MHz, CDCl_3): δ 1.22 (t, 3H, $J=6.8\text{Hz}$, CH_3), 3.78 (s_b, 2H, CH_2N), 4.11 (q, 2H, $J=6.8\text{ Hz}$, OCH_2), 5.19 (m, 3H, $\text{CH}_2=\text{CH}$); ^{13}C NMR (400 MHz, CDCl_3) δ 14.56 (CH_3), 43.81(CH_2N), 60.79 (OCH_2), 115.82 ($\text{CH}_2=$) 134.58 (CH=), 157.47 (CO). Analysis calc'd for $\text{C}_6\text{H}_{12}\text{O}_2\text{N}_1\text{Cl}$: Cald: C 43. 5 H 7. 3 N 8. 5 Found C 43.6 H 7. 4 N 8. 8

Sodium methoxide was prepared¹⁸ by adding, sodium (0.11g, 5mmol) to methanol (20ml) under nitrogen atmosphere and the mixture stirred at room temperature until all the sodium has been used up. To this mixture was added N-phenyl-2-(trimethylsilyl)methyl aziridine (1.0g, 5mmol) and the mixture was then refluxed. Excess methanol was removed by rotatory evaporator, to leave a residue that was taken up in water and extracted using diethyl ether. The organic layer was dried using anhydrous magnesium sulphate. Removal of the solvent and purification over silica gel using with hexane/dichloromethane as the eluent gave N-phenyl allylamine 115 0.48g, (75%).

¹H NMR (400 MHz, CDCl₃) 3.74(d_b, 2H, J= 6.8 Hz, CH₂N), 5.26-5.89 (m, 3H, CH₂=CH), 6.65 and 7.21(m, 5H, Ph) ¹³C NMR (400 MHz, CDCl₃) 46.55 (CH₂N), 116.20(CH₂=), 117.50(=CH), 112.95, 128.92, 135.45, 148.03 (Ph)

A solution of N-phenyl-2-(trimethylsilyl)methylaziridine (0.1g, 0.48mmol) in deuterated chloroform (1ml) was placed in a 5mm nmr. tube. Trimethylsilyltriflate (0.48mmol) was added dropwise. After addition, the nmr. tube was shaken thoroughly and left to stand at room temperature for 5 minutes to give N-phenyl allylamine (98% as determined by ¹H nmr). Attempted purification by column chromatography and distillation on a bigger scale using a Kugelrohr apparatus only gave products of decomposition. Similar reaction conditions as above were employed for trifluoroacetic acid, trifluoromethane sulphonic acid, tetrabutyl ammonium fluoride and boron trifluoride etherate.

To a slurry of dried, purified copper iodide (5mmol) in dry ether (10ml) under nitrogen atmosphere at room temperature was added dropwise N-phenyl-2-(trimethylsilyl)methyl aziridine (5mmol) in dry ether (5ml). The mixture was allowed to stir at room temperature overnight. The solvent was decanted and the slurry washed several times with dry ether. Removal of the solvent, gave a brown liquid which gave a similar ^1H NMR to N-phenyl allylamine. Attempts to purify the crude sample led to decomposition, resulting in unidentified products.

5.12.7

Ring opening reactions with carbon nucleophiles.

5.12.7.1

Reaction of N-phenyl-2-(trimethylsilyl)methylaziridine with methylcuprate.

To freshly dried cuprous iodide (114mg, 0.6mmol) in dry ether (7ml) cooled to 0°C was added methyllithium (0.84ml, 1.4M, 1.2mmol). The solution was stirred at 0°C for 10 mins and at room temperature for 30mins. The cuprate was then cooled to -70°C . To this was added N-phenyl-2-(trimethylsilyl)methylaziridine (102.5mg, 0.5mmol) and the reaction mixture was gradually allowed to warm up to room temperature and stirring continued for another 10hrs. The reaction mixture was then poured into a stirred solution of ammonium chloride in ice. After all the ice has melted, more ether was added and the organic layer extracted, filtered and dried using anhydrous magnesium sulphate. After removal of the solvent using a rotary evaporator, the nmr of the crude product was similar to that of the starting aziridine.

5.12.7.2

Reaction of N-phenyl-2-(dimethylphenylsilyl)methylaziridine with diethylmalonate

Diethylmalonate (0.32g, 0.30ml, 0.002mol) was added dropwise to a stirred suspension of sodium hydride (0.06g, 0.025mol) in 50ml dry THF containing 3ml of HMPA at room temperature. The stirring was continued until evolution of gas ceased. A solution of N-phenyl-2-(dimethylphenylsilyl)methylaziridine (0.27g, 0.001mol) in dry THF (10ml) was then added and the mixture refluxed for 4hrs. The mixture was then allowed to cool to room temperature and THF removed using a rotary evaporator.

The residue was poured into ice water and then extracted with ether. The organic layer was dried over anhydrous magnesium sulphate and concentrated to give a product which had a similar nmr spectrum to the starting aziridine.

5.13

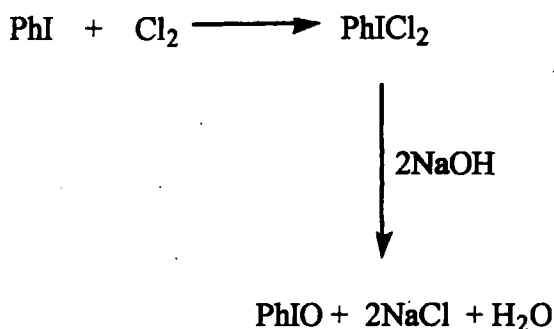
Synthesis of Sultones

Similar reaction conditions were employed for the synthesis of sultones from the reaction of various terminal and internal olefins with the novel electrophilic reagent, iodoso benzene sulfate. This sulfate was synthesized by the sulphonation of iodosobenzene. The synthesis of 2-trimethylsilyl-1, 2-ethane sultone (5.13.3), is representative of the method used in the synthesis.

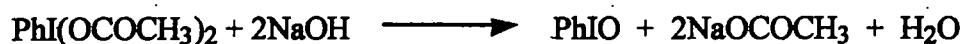
5.13.1

Synthesis of iodosobenzene (PhIO)

Iodosobenzene was prepared by two different literature methods^{19,20}. The first is outlined in the equations below:



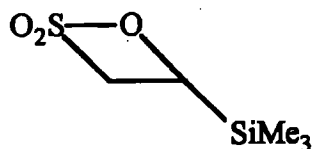
The second method involves the hydrolysis of the readily available iodosobenzene diacetate with aqueous sodium hydroxide.



5.13.2 Synthesis of iodosobenzene sulfate

To a slurry of iodosobenzene (5.50g, 0.025mol) in dry dichloromethane (100ml), at -78°C under a nitrogen atmosphere, was added chlorotrimethylsilylsulfonate ester (3.0ml, 0.02mol) with continuous stirring to produce a clear yellow solution. The reaction mixture was allowed to slowly warm up to room temperature and allowed to stir at this temperature for another 30minutes before removal of the solvent under vacuum, to give a very moisture sensitive yellow solid: m.p. 110°C .; ν_{max} (KBr film/ cm^{-1}) 1580 (Ph), 1295, 1140, 940 (S=O), 560 (I-O), 465 (C-I). MS (EI+) m/e 456 (5.5, - SO_2), 363 (3.7), 330 (12), 237 (6.2), 213 (3.1), 202 (5.5), 149 (16), 126 (6.6), 124 (6.4), 123 (5.9), 111 (19), 109 (8.5), 97 (13), 84 (12), 83 (16), 80 (100), 77 (10), 64 (35), 57 (28), 48 (39), 29 (19). These data are in agreement with published values²¹.

To a slurry of iodosobenzene (2.20g, 0.01mol) in dry dichloromethane (50ml), at -78°C under a nitrogen atmosphere, was added chlorotrimethylsilylsulfonate ester (1.5ml, 0.01mol) with continuous stirring to produce a clear yellow solution. To this was added vinyltrimethylsilane (1.5g, 0.015mol) and the reaction mixture, which turned colourless, was allowed to warm up to room temperature. Stirring was continued at this temperature for another 1hr. Removal of the solvent from the reaction mixture using a rotatory evaporator gave a dark brown tar. Purification of the crude product over silica gel using hexane / dichloromethane as the eluent gave 1.5g (57%) of 2-trimethylsilyl-1,2-ethane sultone **97** as a colourless oil, which readily decomposed after few hours at room temperature.



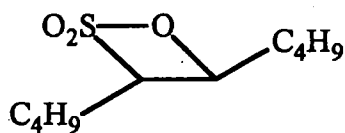
(97)

ν_{max} (neat film/ cm^{-1}) 2957, 2927, 1400, 1254, 1190, 914, 846. ^1H NMR (400 MHz, CDCl_3) δ 0.22 (s, 9H, SiMe_3), 3.88 (dd, 1H, $J_1=6.8\text{Hz}$, $J_2=12.8\text{Hz}$) and 4.06 (dd, 1H, $J_1=4.4\text{Hz}$, $J_2=12.8\text{Hz}$, CH_2S), 4.9 (m, 1H, CHOSO_2 -); ^{13}C NMR (400 MHz, CDCl_3) δ -2.95 (SiMe_3), 43.80 ($\text{CH}_2\text{SO}_2\text{O}$ -), 85.79 (CHOSO_2 -); MS (EI^+) m/e 181 (5.8 (MH^+), 167 (17), 147 (35), 137 (2.3), 116 (4.5), 101 (23), 93 (37), 73 (100), 59 (13), 45 (28), 29 (3). The title compound was very unstable and hence no further analysis could be obtained.

5.13.4

trans-1,2-dibutyl- β -sultone (98)²²

To a slurry of iodosobenzene (2.20g, 0.01mol) in dry dichloromethane (50ml), at -78°C under a nitrogen atmosphere, was added chlorotrimethylsilylsulfonate ester (1.5ml, 0.01mol) with continuous stirring to produce a clear yellow solution. To this was added *trans*-5-decene (2.10g, 0.015mol) and the reaction mixture, which turned colourless, was allowed to warm up to room temperature. Stirring was continued at this temperature for another 1hr. Work-up of the mixture was carried out as described in section 5.14.1 to give 2.14g (65%) of *trans*-1, 2-dibutyl- β -sultone 98 as a colourless oil.



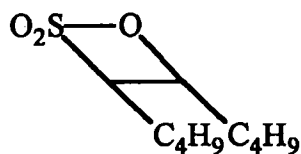
(123)

ν_{\max} (neat film/cm⁻¹) 2959, 2932, 2876, 1455, 1382, 1192, 903. ¹H NMR (400 MHz, CDCl₃) δ 0.94 (m, 6H, 2xCH₃), 1.43-1.96 (m, 12H, (CH₂)₆), 4.2 (dt, 1H, $J_1=9.8$ Hz, $J_2=13.2$ Hz, CHSO₂O-), 4.75 (dt, 1H, $J_1=4.8$ Hz, $J_2=8.8$ Hz, CHOSO₂-); ¹³C NMR (400 MHz, CDCl₃) δ 13.82 (2xCH₃), 22.05, 22.33, 29.16, 29.21, 33.67, 33.80 (6xCH₂), 62.92 (CHSO₂O-), 88.02 (CHOSO₂-); .MS (EI+) m/e 221 (MH⁺), 195 (.7), 177 (4), 175 (2), 157 (1), 139 (10), 95 (17), 87 (60), 83 (17), 69 (100), 57 (20), 55 (26), 45 (9), 43 (25), 41 (52), 29 (2.7), 27 (14).

5.13.5

cis-1,2-dibutyl- β -sultone (99)²²

Reaction of iodosobenzene sulfate (0.01mol) with *cis*-5-decene (0.015mol) gave 1.6g (50%) of *cis*-1,2-dibutyl- β -sultone 99 as a colourless oil



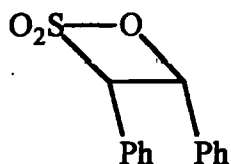
(99)

ν_{\max} (neat film/cm⁻¹) 2959, 2932, 2878, 1456, 1382, 1192, 903. ¹H NMR (400 MHz, CDCl₃) δ 0.90 (m, 6H, 2xCH₃), 1.37-1.84 (m, 12H, (CH₂)₆), 3.61 (dt, 1H, J₁=4Hz, J₂=6.4Hz, CHSO₂O-), 3.90 (dt, 1H, J₁=3.6Hz, J₂=6.8Hz, CHOSO₂-); ¹³C NMR (400 MHz, CDCl₃) δ 13.92 (CH₃), 13.94 (CH₃), 22.22, 22.61, 27.78, 28.82, 34.35, 34.62 (8xCH₂), 69.11 (CH₂SO₂O-), 73.87 (CHOSO₂-). MS (EI+) *m/e* 221 (1.6 (MH⁺)), 195 (1.3), 177 (18), 139 (6), 95 (100), 83 (23), 81 (19), 71 (10), 69 (60), 67 (21), 57 (19), 56 (18), 55 (39), 43 (37), 41(54), 39 (17), 29 (15), 27 (12).

5.13.6

cis-1,2-diphenylsultone (100)

Reaction of iodosobenzene sulfate (0.01mol) with *cis*-stilbene (2.7g, 0.015mol) gave *cis*-1,2-diphenylsultone 100, as a white solid 2.1g(54%) m.pt. 131°C

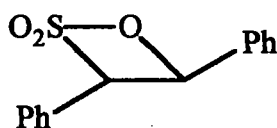


(100)

ν_{max} (neat film/cm⁻¹) 1550, 1475, 1300, 1250, 1200, 1175, 1050, 900, 800, 750, 700, 675, 564, 511. ¹H NMR (400 MHz, CDCl₃) δ 5.21 (s, 1H, CHO), 7.26 (s, 1H, CHS), 7.37-7.45 (m, 10H, 2xPh); ¹³C NMR (400 MHz, CDCl₃) δ 65.69 (CHO), 76.68 (CHS), 128.04, 128.54, 128.99, 138.34 (Ph); MS (EI⁺) m/e 196 (MH⁺ -SO₂ (37)), 195 (40), 178 (20), 168 (17), 167 (70), 165 (25), 152 (17), 105 (100), 90 (60), 89 (66), 77 (58), 64 (11), 63 (22), 57 (6), 51(27), 39 (14), 28 (7); Analysis calc'd for C₁₄H₁₂SO₃: C 64.6, H 4.7; found: C 65.0, H 4.9.

5.13.7 *trans*-1,2-diphenylsultone (101)

Reaction of iodosobenzene sulfate (0.01mol) with *trans*-stilbene (2.7g, 0.015mol) gave *trans*-1,2-diphenylsultone **101**, as a white solid 2.3g, (59%), m. pt. 171°C



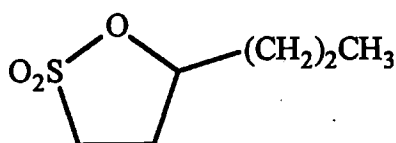
(101)

ν_{max} (neat film/cm⁻¹) 1550, 1475, 1300, 1250, 1200, 1175, 1050, 900, 800, 750, 700, 675, 564, 511. ¹H NMR (400 MHz, CDCl₃) δ 5.22 (s, 1H, CHO), 7.26 (s, 1H, CHS), 7.30-7.45 (m, 10H, 2xPh); ¹³C NMR (400 MHz, CDCl₃) δ 65.69 (CHO), 76.68 (CHS), 128.04, 128.54, 128.99, 138.34 (Ph); MS (EI⁺) m/e 196 (MH⁺ -SO₂ (37)), 195 (40), 178 (20), 168 (17), 167 (70), 165 (25), 152 (17), 105 (100), 90 (60), 89 (66), 77 (58), 64 (11), 63 (22), 57 (6), 51 (27), 39 (14), 28 (7).

5.13.8

3-propyl-1,3-propanesultone (103)^{23,24}

Addition of 1-hexene (1.3g, 0.015mol), to iodosobenzene sulphate generated as described above gave after purification, 1.7g, (68%) of 3-propyl-1,3-propane sultone **103**, as a colorless oil.



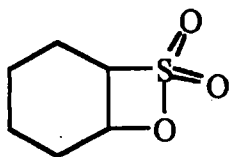
(103)

ν_{max} (neat film/cm⁻¹) 2960, 2931, 1385, 1192, 912. ¹H NMR (400 MHz, CDCl₃) δ 0.93 (t, 3H, CH₃), 1.38-1.87 (m, 4H, (CH₂)₂), 3.72 (dt, 2H, $J_1=4.4\text{Hz}$, $J_2=8.8\text{Hz}$, CH₂CH₂SO₂O-), 3.82 (dt, 2H, $J_1=4.4\text{Hz}$, $J_2=5.6\text{Hz}$, CH₂CH₂SO₂O-), 4.84 (m, 1H, CHOSO₂-); ¹³C NMR (400 MHz, CDCl₃) δ 13.79 (CH₃), 22.26, 26.52, 31.24 (CH₂)₃, 44.57 (CH₂SO₂O-), 84.46 (CHOSO₂-); MS (EI+) m/e 165 (30 (MH⁺)), 149 (4.4), 135 (5.4), 121 (42), 109 (5), 97 (6), 85 (20), 84 (22), 83 (100), 82 (67), 81(22), 71(16), 69 (19), 67 (33), 57 (25), 56 (24), 55 (89), 41 (57), 29 (40).

5.13.9

1,2-cyclohexane sultone (104)

Cyclohexene (0.015mol, 1.2g) was added to iodosobenzene sulfate (0.01mol) generated as described in section 5.13.2, gave a colourless solution which on warming to room temperature turned dark-blue. Purification of the crude mixture over silica gel with hexane /dichloromethane as the eluent gave 1.8g, (69%) of β -sultone **104** as a colorless oil.



(104)

ν_{\max} (neat film/ cm^{-1}) 3000, 2986, 1470, 1225, 987, 946, 770. ^1H NMR (400 MHz, CDCl_3) δ 1.42 (m, 2H, $-\underline{\text{CH}_2}\text{CHO}-$), 1.81(m, 4H, $-\text{CH}_2\text{CH}_2-$), 2.22 and 2.27 (m, 2H, $-\text{CH}_2\text{CHSO}_2-$), 4.04 (m, 1H, $\text{CHSO}_2\text{O}-$), 4.87 (m, 1H, CHOSO_2-); ^{13}C NMR (400 MHz, CDCl_3) δ 22.09, 22.70, 29.65, 33.12 (4x CH_2), 58.58 ($\text{CHSO}_2\text{O}-$), 85.97 (CHOSO_2-); MS (EI+) m/e 162 (0.6), 98 (5, M- SO_2), 81 (100), 80 (49), 79 (25), 77(8), 75(6), 67 (15), 57 (15), 41(29), 39 (14), 29 (9), 27 (11); Analysis calc'd for $\text{C}_6\text{H}_{10}\text{SO}_3$: Cald.: C 44.4 H 6.2; Found: C 44.7 H 6.2.

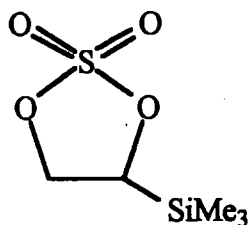
5.14 Synthesis of cyclic sulfates via iodonium ylids.

This section explains in detail the synthesis of the cyclic sulfates mentioned in chapter three, from the reaction of iodosobenzene sulfate with alkenes. Two different procedures (A and B) were used. Similar reaction conditions were used for the synthesis of a range of compounds and hence, the synthesis of 1-trimethylsilylethylene cyclic sulfate is representative.

5.14.1 Trimethylsilyl ethylene-1,2-sulfate (105)

General Procedure A

To a slurry of iodosobenzene (2.20g, 0.01mol) in dry dichloromethane (50ml), at -78°C under a nitrogen atmosphere was added chlorotrimethylsilylsulfonate ester (1.5ml, 0.01mol) with continuous stirring to produce a clear yellow solution. The solution was allowed to slowly warm up to about -10°C and then subjected to vacuum distillation until all the solvent had been removed to leave a yellow powder. A further dry CH_2Cl_2 (50ml) was added and the mixture re-cooled to -78°C . To this was added vinyl trimethylsilane (1.5g, 0.015mol). The reaction mixture, which turned colourless, was allowed to warm up to room temperature and stirring continued at this temperature for another 1hr. Removal of the solvent from the reaction mixture using a rotatory evaporator gave a black residue. Purification of the crude over silica gel using hexane/dichloromethane as the eluent gave 1-trimethylsilylethylene-1,2-sulfate **105** 1.9g, (64%) as a white solid.



(105)

ν_{\max} (KBr film/ cm^{-1}) 2960, 2930, 2857, 1376, 1254, 1202, 943, 843. ^1H NMR (400 MHz, CDCl_3) δ 0.00 (s, 9H, SiMe_3), 4.38 (m, 1H, CHSi), 4.50 (m, 2H, CH_2); ^{13}C NMR (CDCl_3) δ -4.52 (SiMe_3), 72.19 (CH_2), 76.68 (CH); MS (EI^+) m/e 181 (1, M-O^2-), 165 (1), 153 (1), 147 (12), 101 (61), 80 (10), 75 (33), 73 (100), 64 (12), 59 (37), 48 (9), 45 (33), 43 (19), 28 (10). Analysis calc'd for $\text{C}_5\text{H}_{12}\text{Si}_1\text{S}_1\text{O}_4$: Calcd.: C 30. 6 H 6. 2 S 16. 3; Found: C 30. 7 H 5. 7, S 16.2.

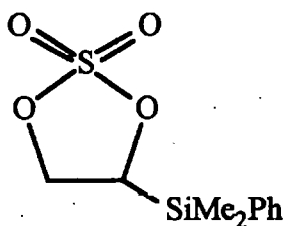
General Procedure B

To 1,4-dioxane (1.32g, 0.015mol,) in dry dichloromethane (25ml), under a nitrogen atmosphere at -5°C was added dropwise chlorotrimethylsulfonate ester (1.5ml, 0.01mol). The reaction mixture was allowed to warm up to room temperature and the solvent removed under vacuum to leave a white crystalline moisture-sensitive solid. To this was added dry dichloromethane (50ml) and the mixture re-cooled to -78°C , before addition of iodosobenzene. The mixture was allowed to warm up to 0°C and vinyltrimethylsilane (1.5g, 0.015mol) was added dropwise. The reaction mixture was allowed to warm up to room temperature and stirring continued at this temperature for another 1hr. Removal of the solvent from the reaction mixture using a rotatory evaporator gave a black residue. Purification of the crude product over silica gel using hexane/dichloromethane as the eluent gave 1-trimethylsilyl-2,3-dioxolane 1,2-dithiolane 1,1-dioxide 105 2.2g, (76%) as a white solid.

The yields recorded for the cyclic sulphates are based on the modified procedure (B).

5.14.2 1-Dimethylphenylsilyl-ethylene-1,2-sulfate (106)

Reacting the electrophilic reagent generated insitu as described in 5.14.1(B), with 1.62g (0.01mol) of vinyl dimethylphenylsilane gave 1-Dimethylphenylsilyl-ethylene-1, 2-sulfate **106**, 0.7g,(65%) as a white solid.

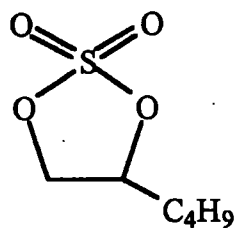


(106)

ν_{\max} (KBr film/ cm^{-1}) 2960, 1375, 1254, 1200, 1119, 935, 852, 832. ^1H NMR (400 MHz, CDCl_3) δ 0.52 (s, 3H, SiMe), 0.53 (s, 3H, SiMe), 4.52 (dd, 1H, $J_1=8.8\text{Hz}$, $J_2=12\text{Hz}$, CH_2), 4.56 (dd, 1H, $J_1=6.4\text{Hz}$, $J_2=8.8\text{Hz}$, CH_2), 4.86 (dd, $J_1=6.4\text{Hz}$, $J_2=12\text{Hz}$, CH), 7.54 (m, 5H, Ph); ^{13}C NMR (400 MHz, CDCl_3) δ -6.5, -5.5 (SiMe₂), 72.37 (CH_2), 77.48 (CHSi), 128.7, 130.99, 131.75, 134 (Ph); MS (FAB) m/e 259 (23), 258 (51), 257 (30), 123 (51), 96 (94), 80 (100), 64 (22). This product was very unstable and hence could not be characterised further.

5.14.3 1-*n*-butylethylene-1,2-sulfate (107)

Addition of 1-hexene (1.3g, 0.015mol), to iodosobenzene sulphate, generated as described above (procedure B), gave after purification, 1.8g (66%) of 1-*n*-butylethylene-1,2-sulfate **107**.

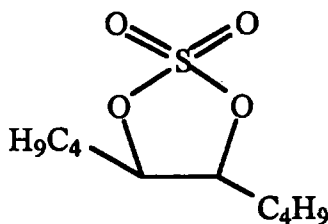


(107)

ν_{\max} (neat film/ cm^{-1}) 2962, 2936, 1469, 1387, 1212, 1191, 997, 832. ^1H NMR (400 MHz, CDCl_3) δ 0.95 (t, 6H, $J=6.8\text{Hz}$, CH_3), 1.26-2.1 (m, 6H, $(\text{CH}_2)_3$), 4.33 (dd, 1H, $J_1=5.3\text{Hz}$, $J_2=12.2\text{Hz}$, CH_2O), 4.75 (dd, 1H, $J_1=7.5$, $J_2=12.2$, CH_2O) 5.12 (m, 1H, CHO); ^{13}C NMR (400 MHz, CDCl_3) δ 13.83 (CH_3), 22.15, 26.56, 32.12 (CH_2)₃, 72.86 (CH_2O), 83.30 (CHO); MS (EI^+) m/e 181(2, (MH^+)), 164 (7.8), 149 (3), 139 (3.4), 129 (6), 123 (10), 100 (13), 87 (16), 83 (100), 82 (69), 81 (19), 71 (20), 69 (30), 67 (49), 57 (26), 55 (66), 44 (23), 43 (37), 41 (61), 39 (14), 29 (41), 27 (20). Analysis calc'd for $\text{C}_6\text{H}_{12}\text{SO}_4$: Calcd.: C 40.0 H 6.7; Found: C 40.6, H 6.8.

5.14.4 1,2-*n*-dibutylethylene cyclic sulfate (108)²⁵

Reacting the sulfonating reagent with *cis*-5-decene (0.70g, 0.005mol), gave, (50%) 1,2-*n*-dibutylethylene cyclic sulfate, 108 0.6g, (50%).

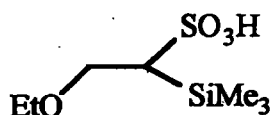


(108)

^1H NMR (400 MHz, CDCl_3) δ 0.93 (t, 6H, $J=6.84\text{Hz}$, $2\times\text{CH}_3$), 1.35-1.39 (m, 12H, $(\text{CH}_2)_6$), 4.89 (dd, 2H, $J_1=2.96\text{Hz}$, $J_2=6.84\text{Hz}$, $2\times\text{CH}$); ^{13}C NMR (400 MHz, CDCl_3) δ 13.76 (CH_3), 22.15, 27.31, 28.09 ($3\times\text{CH}_3$), 86.19 (CH).

5.14.5 1-Trimethylsilyl-2-ethoxyethane sulfonic acid (111)

To a slurry of iodosobenzene (2.20g, 0.01mol) in dry dichloromethane, (50ml) at -78°C under a nitrogen atmosphere was added chlorotrimethylsilylsulfonate ester (1.5ml, 0.01mol) with continuous stirring to produce a clear yellow solution. The solution was allowed to slowly warm up to about -10°C and then subjected to vacuum distillation. When all the solvent had been removed, a yellow powder remained. A further 50ml of dry CH_2Cl_2 "spiked" with ethanol was added and the mixture re-cooled to -78°C . To this was added vinyltrimethylsilane (1.5g, 0.015mol) and the reaction mixture, which turned colourless, was allowed to warm up to room temperature and stirring continued at this temperature for another 1hr. Removal of the solvent from the reaction mixture using a rotatory evaporator gave a black residue. Purification of the crude product over silica gel using hexane/dichloromethane as the eluent gave an oil, 111 2.2g, (65%).



(111)

ν_{max} (neat film/ cm^{-1}) 2986, 1388, 1254, 1192, 923, 848. ^1H NMR (400 MHz, CDCl_3) δ 0.00 (s, 9H, SiMe_3), 1.42(t, 3H, $J=6.8\text{Hz}$, CH_3), 3.87 and 4.02(dd, 1H, $J_1=6.4\text{Hz}$, $J_2=12.8\text{Hz}$ and dd, 1H, $J_1=3.6\text{Hz}$, $J_2=12.8\text{Hz}$, CH_2 -), 4.67 (dd, 1H, $J_1=3.6\text{Hz}$, $J_2=6.4\text{Hz}$, CHO); ^{13}C NMR (400 MHz, CDCl_3) δ -2.83 (SiMe_3), 14.51 (CH -), 44.85 (CH_2O -),

69.95 (OCH_2CH_3), 80.89 (CHO); MS (EI^+) m/e 225 (1, (M-H)), 197 (4), 181(1), 167 (4), 155 (17), 152 (7), 147 (3), 139 (4), 124 (17), 117 (6), 103 (10), 93 (23), 75 (56), 73 (100), 59 (12), 45 (22), 44 (20), 43 (17), 29 (28), 27 (11)

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